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Article

A nanocrystalline MgO support for Ni catalysts for steam reforming of CH₄

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ABSTRACT

Nanocrystalline MgO with a relatively high surface area and mesoporous structure was synthesized by a surfactant assisted precipitation method for use as the support of nickel catalysts for steam reforming of methane. The samples were characterized by X-ray diffraction, N₂ adsorption, temperature-programmed reduction, temperature-programmed oxidation, scanning electron microscopy, and transmission electron microscopy. The catalysts showed high catalytic activity and good stability in the steam reforming of methane. Increasing the nickel loading up to 10 wt% gave increased activity. Catalysts with higher nickel loadings showed more deposited carbon after reaction. The excellent anti-coking performance of the catalysts was attributed to the formation of a nickel-magnesia solid solution, basicity of the support surface, and nickel-support interaction.

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1. Introduction

The reforming of methane with steam is used in industry for synthesis gas production [1]. In this process, different catalysts have been used. Deactivation of nickel catalysts as a result of carbon deposition is a main problem in this process [2]. Although carbon deposition is affected by many factors, the two important properties are surface acidity and surface structure. Coke formation on larger nickel particles occurs easily, which deactivates nickel active sites. In addition, acidic supports can lead to carbon deposition.

It has been suggested that the use of a catalyst support with a low concentration of Lewis acid sites would decrease coke formation [3,4]. MgO is widely selected as a catalyst support because of its high thermal stability and low cost [5–8]. The surface areas of metal oxide powders at high temperatures depend on their melting point and occurrence of phase trans-

formation. MgO has a very high melting point (2850 °C), which can allow MgO to maintain a relatively large surface area at high temperatures when compared to most other oxides used as a catalyst support. Furthermore, MgO and NiO both have a face centered cubic structure with almost the same lattice parameters, 4.2112 Å for MgO and 4.1684 Å for NiO. As a result, the interaction of MgO and NiO leads to the formation of a solid solution (NiO-MgO) [8], on which only a small amount of NiO in the solid solution can be reduced, leading to very small Ni particles. The very small sized Ni particles play an important role in inhibiting carbon deposition [9]. Therefore MgO with high basicity would be an appropriate support to prevent coke formation. In this work, plate-shaped nanocrystalline MgO with a high surface area was synthesized and used as the support for nickel catalysts for the steam reforming of methane.

2. Experimental

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2.1. MgO preparation

Polyvinyl alcohol (PVA, $M_r = 72000$) was dissolved in water at 90 °C under vigorous stirring to form a transparent solution. $Mg(NO_3)_2 \cdot 6H_2O$ was dissolved in this solution. The metal ion to PVA monomer molar ratio (Mg/PVA) was 1:3. Aqueous ammonia (25 wt%) was added dropwise at room temperature to the resulting viscous liquid mixture under rapid stirring and careful pH adjustment to 10.5. After precipitation, the slurry was stirred for another 30 min and then refluxed at 80 °C for 20 h under continuous stirring. The mixture was cooled to room temperature, filtered, and washed with hot deionized water to remove polyvinyl alcohol. The final product was dried at 80 °C for 24 h and calcined at 700 °C for 4 h.

2.2. Catalyst preparation

Ni catalysts supported on MgO were prepared by impregnation using an aqueous solution of $Ni(NO_3)_2 \cdot 6H_2O$. After impregnation, the sample was dried at 80 °C and calcined at 500 °C for 4 h in static air atmosphere.

2.3. Characterization

The surface areas (BET) were determined by nitrogen adsorption at –196 °C using an automated gas adsorption analyzer (Tristar 3020, Micromeritics). The X-ray diffraction (XRD) patterns were recorded on an X-ray diffractometer (PANalytical X'Pert-Pro) in the range $2\theta = 10^\circ$ – 80° . Temperature-programmed reduction (H_2 -TPR) was performed in an automatic apparatus (Chemisorb 2750, Micromeritics) equipped with a thermal conductivity detector (TCD). The fresh catalyst (200 mg) was pretreated with a heat treatment (10 °C/min) in a gas flow (40 ml/min) of 10% H_2 /Ar. Temperature-programmed oxidation (TPO) of spent catalysts was performed in the same apparatus by introducing a gas flow (30 ml/min) of 5% O_2 /He over 50 mg of spent catalyst and the temperature was increased at a heating rate of 10 °C/min. Surface morphology of the samples was investigated by scanning electron microscopy (SEM, Vega@Tescan) and transmission electron microscopy (TEM, JEOL JEM-2100UHR).

2.4. Catalyst evaluation

Activity measurements were carried out in a fixed-bed continuous flow reactor made of 7 mm i.d. quartz tube at atmospheric pressure. The reactor was charged with 200 mg catalyst. Prior to the reaction, the catalyst was reduced at 750 °C for 8 h in flowing H_2 (30 ml/min) and cooled to 600 °C in a flow of Ar (30 ml/min). After that, a reactant gas consisting of a mixture of CH_4 and steam was introduced into the reactor, and the activity test was performed at temperatures ranging from 600 to 750 °C in steps of 50 °C with 60 min at each temperature. The loss in catalyst activity at 700 °C was monitored for 50 h time on stream. The gas composition of reactants and products was analyzed using a gas chromatograph equipped with a TCD and a Carboxen 1000 column.

Fig. 1. XRD patterns of calcined Ni/MgO catalysts and MgO support.

3. Results and discussion

Figure 1 shows the XRD pattern of the synthesized MgO powder. All the XRD peaks can be assigned to pure periclase MgO phase. The lattice parameter of MgO was $a = 4.21 \text{ \AA}$, in good agreement with JCPDS PDF data (No. 45-946) [10]. In the XRD patterns of the Ni/MgO catalysts in Fig. 1, the peaks assigned to NiO and MgO in the 10% Ni+90% MgO physical mixture changed into one peak for 10% Ni/MgO, indicating the formation of a solid solution of NiO and MgO. The XRD patterns of the catalysts with 5% and 7% nickel also showed one peak at 74.5° , indicating the formation of a NiO-MgO solid solution. The increasing intensity of the diffraction peaks with increasing nickel content indicated that there was an increase in the crystallite size of the solid solution.

The structural properties of the Ni/MgO catalyst support and calcined Ni/MgO catalysts are presented in Table 1. The MgO catalyst support showed a relatively high surface area and nanocrystalline structure. The specific surface area decreased with increasing Ni content for catalysts with nickel loadings higher than 7%. The N_2 adsorption profiles for the calcined Ni/MgO catalysts are shown in Fig. 2(a). The N_2 isotherms were type IV with a large type H_3 hysteresis loop. This type of hysteresis is usually found with solids consisting of agglomerates of particles that form slit shaped pores (plates or particles with edges, like cubes) with a non-uniform size and/or shape. The

Table 1

Structural properties of the catalyst support MgO and Ni/MgO catalysts.

Sample	A_{BET} (m^2/g)		Pore volume (cm^3/g)		Pore size (nm)	
	Fresh	Spent	Fresh	Spent	Fresh	Spent
MgO	72.4	—	0.19	—	15.2	—
5% NiO/MgO	44.4	28.3	0.24	0.23	12.1	16.0
7% NiO/MgO	63.4	23.0 ^a	0.23	0.18 ^a	14.6	22.8 ^a
10% NiO/MgO	51.5	40.7	0.26	0.18	12.5	16.1
15% NiO/MgO	46.5	27.7	0.26	0.24	12.9	17.7

^aSpent catalyst after 50 h time on stream.

Fig. 2. N₂ adsorption isotherms (a) and pore size distributions (b) of the Ni/MgO catalysts.

pore size distribution of the samples is shown in Fig. 2(b). The samples had mesoporous structure with a pore size distribution in the range of 12–14 nm.

The SEM images of the MgO sample calcined at 700 °C showed a plate shape and nanocrystalline structure (Fig. 3(a)). The SEM analysis also showed that the MgO consisted of irregularly shaped quasi-two dimensional micron-sized particles. The TEM analysis also confirmed that the MgO crystals were plate-like in shape (Fig. 3(b)).

Figure 4 presents the H₂-TPR results of the catalysts. The TPR profiles of calcined catalysts showed a small reduction peak at around 500 °C, which was due to some Ni²⁺ ions in a square pyramidal coordination in the outmost layer of the MgO

structure. The major reduction peak was observed at a very high temperature, around 1000 °C, which was ascribed to the reduction of Ni²⁺ ions located in the subsurface layers of the MgO lattice. This showed that there was a strong interaction between NiO and MgO and formation of a NiO-MgO solid solution. In addition, the intensity of the first small peak at 500 °C was weaker in catalysts with lower nickel contents, indicating that most of the nickel was incorporated into the MgO structure to form a solid solution. The TPR results and analysis were in agreement with the XRD results, which showed the formation of a NiO-MgO solid solution.

CH₄ conversion over the Ni/MgO catalysts with various nickel loadings at different reaction temperatures is shown in Fig. 5(a). The CH₄ conversion increased with increasing reaction temperature. There was an increase in methane conversion with increasing Ni content up to 7%. With increasing Ni content that was more than 7%, the methane conversion decreased due to a lower nickel dispersion on the catalyst surface. This suggested that the higher Ni loading increases the Ni particle size and subsequently diminishes the active sites for CH₄ conversion. Fig. 5(b) indicates that all the catalysts have stable activity at 700 °C during 6 h time on stream.

The effect of gas hourly space velocity (GHSV) on the catalytic performance of 7% Ni/MgO catalyst was investigated. The

Fig. 3. SEM (a) and TEM (b) images of the MgO support.

Fig. 4. H₂-TPR profiles of the Ni/MgO catalysts.

Fig. 5. CH₄ conversion (a) and catalyst stability (b). (1) 5% Ni/MgO; (2) 7% Ni/MgO; (3) 10% Ni/MgO; (4) 15% Ni/MgO. CH₄/steam = 1 and GHSV = 3.6×10^4 ml/(h·g).

Fig. 6. Effect of GHSV (a) and H₂O/CH₄ ratio (b) on the catalytic conversion of 7% Ni/MgO catalyst. Reaction temperature = 700 °C.

results are presented in Fig. 6(a). CH₄ conversion decreased with increasing GHSV, because a larger GHSV gave less contact time.

In addition, the effect of the H₂O/CH₄ ratio on the catalytic performance of the 7% Ni/MgO catalyst was investigated (Fig. 6(b)). Increasing the H₂O/CH₄ ratio increased the methane conversion. This was due to the decreasing of the amount of oxidant (H₂O).

Figure 7 shows the long term stability of the 7% Ni/MgO catalyst. The catalyst showed good catalytic stability during 50 h on stream.

Figure 8(b) shows the pore size distribution of spent catalysts after 6 h time on stream. Mesoporosity was still seen in the spent catalysts. However, the pore size distribution of the 7% Ni/MgO catalyst was shifted to larger pores after 50 h time on stream. The N₂ isotherms were type IV with a large Type H₃ hysteresis loop that is due to mesoporous structure (Fig. 8(a)). Furthermore, the specific surface area of the spent catalysts had decreased as compared to the fresh catalysts, as presented in Table 1. In addition, there was a decrease in pore volume and increase in the pore size of the catalysts after reaction.

The SEM analysis of the spent catalysts is shown in Fig. 9. The results revealed that deposited carbon increased with increasing nickel content, and the most amount of deposited

carbon was observed on 15% Ni/MgO.

The TPO profiles of the spent Ni/MgO catalysts with different nickel loadings are shown in Fig. 10. The results showed an increase in the intensity and area of the peaks in the TPO profiles with increasing nickel content. The results indicated three kinds of carbon species on the catalyst surface after the steam reforming reaction. The first peak at 150–200 °C can be as-

Fig. 7. Long term stability of 7% Ni/MgO. H₂O/CH₄ = 1, GHSV = 1.83×10^4 ml/(h·g), reaction temperature = 700 °C.

Fig. 8. N₂ adsorption isotherms (a) and pore size distributions (b) of spent Ni/MgO catalysts.

Fig. 9. SEM analysis of the spent Ni/MgO catalysts with different nickel loadings. (a) 7% Ni/MgO; (b) 10% Ni/MgO; (c) 15% Ni/MgO.

signed to superficial carbidic carbon (C_α) [8,9,11]. The second peak at 400 °C was assigned to amorphous carbon on the nickel site [12] and the third peak at temperatures higher than 500 °C was assigned to whisker-type carbon [12–15]. The most amount of carbon deposition was observed on the 15% Ni/MgO catalyst.

Fig. 10. TPO analysis of spent Ni/MgO catalysts with different nickel loadings.

4. Conclusions

Nanocrystalline MgO with a plate-like shape that had a relatively high surface area and highly defective surface structure was employed as the support of Ni catalysts for steam reforming. The strong interaction between NiO and MgO in the solid solution inhibited the reduction of NiO. Thus, relatively small and highly dispersed metallic Ni particles were obtained in the reduction treatment. The metal surface was more resistant towards coke formation because the ensemble size necessary for carbon formation is larger than the ensemble size necessary for methane reforming. An increase in nickel content gave an increased amount of deposited carbon. The 7% Ni/MgO catalyst was very effective in methane steam reforming and exhibited stable activity up to 3000 min of reaction.

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Graphical Abstract

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A 7% Ni catalyst supported on mesoporous nanocrystalline MgO showed high catalytic stability and low degree of carbon formation in steam reforming of methane for syngas production.

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