Original paper

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Ni-containing catalysts based on ordered mesoporous $\text{MgO-Al}_2\text{O}_3$ for methane dry reforming

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Abstract: The ordered mesoporous Mg- and Ni-Mg-alumina samples of general formula $x\text{wt}\%\text{Mg-Al}_2\text{O}_3$ and $y\text{wt}\%\text{Ni-}x\text{wt}\%\text{Mg-Al}_2\text{O}_3$ ($x, y = 5, 10\%$ wt) have been prepared by the one-pot evaporation induced self-assembly (EISA) method using Pluronic P123 as a template. The textural and structural properties of the prepared samples have been characterized by N_2 adsorption-desorption analysis, BET, XRD, TEM with EDX, HAADF-STEM, and H_2 -TPR. The samples calcined at 700°C had an ordered mesoporous structure with a SSA of $170\text{--}250\text{ m}^2/\text{g}$, a pore volume of $0.5\text{--}0.64\text{ cm}^3/\text{g}$ and a narrow distribution of the pore size (mean $12\text{--}16\text{ nm}$). For the catalysts prepared by the one-pot EISA method, the size of the metal Ni particles was in the range of $3\text{--}12\text{ nm}$ and was conditioned by their confinement in the mesopores and the interaction with MgO and Al_2O_3 . Testing in methane dry reforming in the $15\text{v}\%\text{CH}_4 + 15\text{v}\%\text{CO}_2$ feed, with He balance, at $650\text{--}750^\circ\text{C}$ and the contact time of 0.015 s has shown the higher activity and stability of the ordered mesoporous $10\text{w}\%\text{Ni-}10\text{w}\%\text{Mg-Al}_2\text{O}_3$ catalysts prepared by the one-pot method as compared with the catalyst of the same composition obtained by impregnation.

Keywords: methane dry reforming, nickel, mesoporous $\text{MgO-Al}_2\text{O}_3$ supports, synthesis, catalytic activity, coking stability, sintering.

1 Introduction

Recently, methane dry reforming (MDR) has attracted considerable attention as a process generating synthesis gas with a H_2/CO ratio close to unity – a favorable feedstock for the production of oxygenates and liquid hydrocarbons in the Fischer–Tropsch synthesis [1–3].

Ni-containing catalysts possessing a high initial activity are promising for this practical application due to their low cost. The drawbacks of these catalysts are the sintering of the nickel and heavy coking. It is reported in the literature that sintering of Ni particles could be prevented by strong interaction with a substrate when Ni-containing perovskites, spinel and fluorite-like solid solutions are used as precursors of the catalysts [4, 5]. Furthermore, in such systems Ni particles formed *in situ* under reducing conditions have a small size that suppresses carbon formation linked with the ensemble effect [5–7]. However, they have a low specific surface area (SSA) and small pore volume that prevents their wide practical application.

Another approach to improve the activity and stability of Ni-catalysts in methane dry reforming is the use of supports of a high surface area, especially mesoporous supports which have an advantage over traditional supports due to a combination of a high specific surface area, a large pore volume and an ordered pore structure [8]. Recently, it was found that supporting of nickel on mesoporous supports such as SiO_2 [9–11] or $\gamma\text{-Al}_2\text{O}_3$ [12–14] provides control of the Ni particle size and prevents sintering under reaction conditions owing to a confinement of the metal particles within structured pores, thus ensuring a high catalyst stability. Furthermore, it is known that alkali-earth elements such as Mg and Ca improve the activity and stability of Ni-based catalysts supported on the usual $\gamma\text{-Al}_2\text{O}_3$ in methane reforming reactions [15–16]. Their positive effect is commonly attributed to the decrease of the concentration of Lewis centers on the surface of $\gamma\text{-Al}_2\text{O}_3$ promoted with basic Mg(Ca) cations that facilitates

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the adsorption and dissociation of acidic CO_2 and its reaction with carbon deposits. In addition, the growth of Ni particles could be prevented by an interaction with alumina and MgO resulting in the formation of Ni-Mg-Al spinels and NiO-MgO solid solutions as well, which depends to a large extent on the catalyst preparation method and Mg concentration [17-18]. Thus, the one-pot method for preparation of ordered mesoporous NiO-MgO- Al_2O_3 catalysts could be more efficient than a common impregnation of mesoporous Al_2O_3 with appropriate solutions. The formation of a NiO-MgO solid solution during synthesis and the subsequent segregation of Ni metal nanoparticles within the mesopores of Al_2O_3 could also provide high activity and stability of catalysts [19-21].

In the present work, the ordered mesoporous NiO-MgO- Al_2O_3 catalysts have been prepared by the known one-pot evaporation-induced self-assembly (EISA) with block copolymers method [12-14, 19] and, for comparison, by impregnation. The influence of the preparation method and Mg and Ni concentrations on the textural and structural properties of synthesized catalysts, and their activity and stability during methane dry reforming has been studied.

2 Experimental

2.1 Synthesis of ordered mesoporous supports and catalysts

Mesoporous pure alumina was synthesized using an EISA method [12, 13]. In a typical synthesis, 2.0 g of $(\text{EO})_{20}(\text{PO})_{70}(\text{EO})_{20}$ triblock copolymer (Pluronic P123, $M_n=5800$, Sigma Aldrich) was dissolved in 20.0 mL of 99.9% anhydrous ethanol (J.T. Baker) with stirring for 1 h at room temperature. 4.08 g of aluminum isopropoxide (Acros Organics) was dissolved in 3.2 mL 60 wt % nitric acid (Reahim) and 10.0 mL anhydrous ethanol. Then, these two solutions were combined and the resulting solution,

covered by a PE film, was stirred at room temperature for 4 hours. Evaporation of solvent was carried out at 60 °C for 48 h in air without stirring.

Synthesis of the Mg- and Ni-Mg-alumina samples of general formula $x \text{ wt\%Mg-Al}_2\text{O}_3$ and $y \text{ wt\%Ni-x wt\%Mg-Al}_2\text{O}_3$ ($x, y = 5, 10 \text{ \% wt}$) designated as $y\text{Ni}x\text{MgAl-op}$ was performed using a one-pot EISA method [13, 19-21] similar to that for the pure alumina described above. The amounts of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and/or $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ required for the given sample composition were added to the solution of Pluronic P123 in anhydrous ethanol, and then all procedures were the same as for the synthesis of pure alumina. All samples after drying at 60 °C were calcined with a heating rate of 1 °C/min up to 700 °C in a horizontal quartz tube furnace under air flow and kept at the final temperature for 5 hours.

For comparison, samples containing 10 wt% Ni were prepared by incipient impregnation of mesoporous supports 5Mg5MgAl (5Mg-Al (one-pot) additionally impregnated with Mg) using solutions of $\text{Ni}(\text{NO}_3)_2$ or $\text{Mg}(\text{NO}_3)_2$. The sample is designated as 10Ni5Mg5MgAl-im.

The composition and some characteristics of mesoporous samples are presented in Table 1.

2.2 Characterization techniques

The samples were characterized by N_2 adsorption-desorption isotherms, BET, XRD, TEM with EDX, and H_2 temperature-programmed reduction. Nitrogen adsorption-desorption measurements were carried out at 77 K using an ASAP 2400 (Micromeritics) apparatus. BET specific surface area (SSA, m^2/g) was determined from the data on Ar thermodesorption. X-ray diffraction patterns at small angles were recorded using a D500 diffractometer (Siemens) from 2θ of 0.5 to 5.0° with a step size 0.02° and a count time 40s. XRD patterns at wide angles were obtained with a D8 Advance diffractometer (Bruker) in a 2θ scanning range of $10-80^\circ$ with a step of 0.05° and a

Table 1. Composition and textural characteristics of mesoporous samples

Sample	SSA _{BET} , m^2/g	V_{total}^a , cm^3/g	d_{pore}^b , nm
Al_2O_3	242	0.52	13.5
5MgAl-op	220	0.51	12
10MgAl-op	251	0.64	16
5Ni5MgAl-op	205		
10Ni10MgAl-op	183		
10Ni(5Mg(5Mg-op))-im	170		

count time of 3 s. CuK α radiation ($\lambda=0.15418$ nm) was used in both cases.

The TEM micrographs were obtained with a JEM-2010 instrument (lattice resolution 1.4 Å and acceleration voltage 200 kV). Local elemental analysis was performed with an EDX method (a Phoenix Spectrometer).

The redox properties of the initial samples were studied using temperature-programmed reduction (TPR) by H₂ (10% H₂ in Ar, the feed rate 2.5 L/h, the temperature ramp from 25 to 900 °C at 10°/min). The experiments were carried out in kinetic installations equipped with a GC Tcvt-500.

Methane dry reforming (MDR) was studied in a tubular plug-flow reactor (15v.% CH₄+ 15v.%CO₂, He balance, at 650-750°C and contact time 0.015 s (GHSV 240000 h⁻¹). Before testing, catalysts were reduced in a feed of 5% H₂ in He at 650 °C. The experiments were conducted successively at increasing, and then at decreasing temperature. The concentrations of reactants and products were analyzed by on-line IR absorbance, electrochemical, and polarographic gas sensors for different components.

3 Results and discussion

3.1 Textural and structural properties

The textural features of samples calcined at 700 °C were studied using nitrogen physisorption at 77 K. The N₂ adsorption and desorption isotherms for pure alumina, and the one pot samples 5MgA-op and 10MgA-op are shown in Fig. 1. According to the classification adopted by IUPAC, all isotherms belong to type IV isotherms with H1 and H2 shaped hysteresis loops, which are the features of ordered mesoporous materials [9, 12]. The hysteresis

loops for pure alumina and 5MgA-op are H2 shaped while an H1-shaped hysteresis loop is observed for the sample 10MgA-op. The H1 hysteresis loop with a steep capillary condensation step at $P/P_0 \sim 0.6$ is usually associated with 2D hexagonal cylindrical-like pore channels. The H2 shaped hysteresis loops are evidence that the pure alumina and 5MgA-op have also 2D hexagonal symmetry but with some structure disordering and, additionally, some of their cylindrical pores may have internal porous plugs [22]. The pore size distribution for the pure alumina and the sample 5MgA-op is narrow with maxima at 5.44 and 6.5 nm pore size, respectively (Fig. 1). At increasing Mg content up to 10 wt% (the sample 10MgA-op), a broad shoulder with a maximum at ~ 9 nm appears, thus leading to a larger mean pore size as compared with those for the pure alumina and 5MgA-op (Table 1). The difference in the porous structure of the samples could be due to the influence of the magnesium and nickel cations on the EISA process. It is known that the ordered mesopores in one pot samples arise from the ordered micelle structures of the organic template, and are affected by its subsequent removal during calcination. Thus, the presence of Mg and Ni cations and their concentration could affect the size of template micelle rods and, therefore, the pore size in the final samples [12-14]. After calcination at 700 °C both the pure sample and those doped with Mg alumina have a high SSA ~ 220 -250 m²/g, the addition of Ni leads only to a slight decrease (180-205 m²/g) (Table 1), which shows a high thermal stability of the ordered mesoporous structure.

The X-ray diffraction at small angles (SAXRD) allows additional information on the ordered mesoporous structures to be obtained. Note that for these materials, the SAXRD peaks arise from the walls of the ordered channels in the framework, they are not characteristics of the crystal

Fig. 1. Adsorption-desorption isotherms (right) and pore size distribution (left) for pure (1) and Mg-doped Al₂O₃ (2 - 5% and 3 - 10% Mg) calcined at 700°.

lattice [9]. The SXRD patterns for the pure alumina and the one-pot samples with 5wt%Ni and/or 5wt%Mg calcined at 700 °C are presented in Fig. 1. Two reflections at $\theta \sim 0.7^\circ$ and $\sim 1.5^\circ$ correspond to the [100] and [110] plane of the 2D hexagonal structure (p6 mm symmetry) [12, 13]. Though the intensity of these SXRD peaks depends on the sample's composition, being the most pronounced for 5MgA-op, their presence for another sample implies that they are ordered but, in accordance with adsorption data, their structural ordering is reduced. The XRD patterns at wide angles are similar for the pure alumina and one-pot samples 5MgA-op and 5Ni5MgA-op (Fig. 2). There are only broad reflections of low intensity corresponding to γ - Al_2O_3 of a low crystallinity. The reflections of MgO or NiO are

absent, which could have resulted from their interaction with alumina and/or their high dispersion.

TEM investigation has been performed for the additional study of the samples' mesoporous structure. Typical images of the pure alumina and the doped sample 5Ni5MgA-op calcined at 700°C are presented in Fig. 3. For both samples, the ordering of cylindrical pores along [110] and [001] directions with a 2D hexagonal p6 mm structure is observed thus confirming the adsorption and SXRD data.

To study the influence of the preparation method on the size of metal nickel particles in catalysts prepared by the one-pot EISA method and by common impregnation we use HRTEM with EDX and HAADF-STEM. The

Fig. 2. Small (left) and wide (right) angles XRD patterns for pure Al_2O_3 (1) and Ni-Mg-doped Al_2O_3 (2 - 5% Mg and 3 - 5%Ni+5%Mg) calcined at 700°C.

A

B

Fig. 3. TEM image of mesoporous samples: pure Al_2O_3 (A) and initial 5%Ni+5%Mg- Al_2O_3 prepared by one-pot method (B).

TEM images of the reduced catalysts 10Ni10MgAl-op and 10Ni5Mg5MgAl-im prepared by the incipient impregnation of 5Mg(5MgAl-op) sample obtained by impregnation with magnesium nitrate of 5MgAl-op support are presented in Fig. 4. It is clearly seen that in the case of 10Ni5Mg5MgAl-im, the nickel particles are located on the surface of the structured 5Mg(5MgAl-op) support, and their size is substantially larger than those for 10Ni10MgAl-op. Furthermore, according to EDX data (Table 2), the distribution of metal particles for the sample 10Ni5Mg5MgAl-im is nonuniform, which is usual for the catalysts prepared by impregnation. The TEM image of reduced 10Ni10MgAl-op shows small particles of 3-12 nm size while HAADF-STEM evidences their uniform distribution over the catalyst (Fig. 4). Additionally, the size of metal nickel particles corresponds to the pore size of the structured mesoporous supports prepared by the one pot method (Table 1, Fig.1).

3.2 H_2 -TPR

The H_2 -TPR spectra for the catalysts are presented in Fig. 5. The H_2 -TPR profiles for the one-pot catalysts 5Ni5MgA-op and 10Ni10MgAl-op are intensive practically symmetric lines with the maxima at 670 and 715°C having a small shoulder at ~ 825°C. First of all, it should be noted that the absence of hydrogen consumption in the region of ~ 400-450°C evidences the absence of pure NiO phase due to the interaction of the nickel with a support [15-18]. The main hydrogen consumption depending on the Ni concentration corresponds to reduction of the NiO-MgO

solid solution which is directly formed in the course of one-pot synthesis followed by calcination at 700 °C [20, 21]. A slight hydrogen consumption at higher temperature, which could be assigned to the reduction of NiAl_2O_4 , is more marked for 5Ni5MgA-op. For the 10Ni5Mg5MgA-im catalyst prepared by the impregnation, the H_2 -TPR profile is a broad asymmetric peak with the maximum at 745°C, a long “tail” in the range of 300-600°C and a shoulder at 840 °C (Fig. 5). The low temperature consumption of hydrogen is due to the reduction of a NiO phase, while consumption at higher temperatures corresponds to the reduction of the NiO-MgO and NiAl_2O_4 mixed oxides.

It is known that a broad H_2 -TPR profile is usually evidence that precursors of Ni-metal particles have a different nature and size resulting in a wide range of Ni⁰ particle sizes. Narrow H_2 -TPR profiles are observed for the reduction of nickel-containing species with a narrow size distribution resulting in a narrow distribution of Ni metal particles [23]. Thus, the narrow H_2 -TPR profiles for the one-pot samples show a narrower size distribution

Table 2. EDX data on the elemental distribution within selected areas for the sample 10Ni5Mg5MgAl-im reduced at 650°C.

Area	Atomic %		
	Mg	Al	Ni
1	9.71	85.68	4.61
2	19.43	0.47	80.10
3	20.76	2.13	77.11
4	26.69	7.72	65.60
5	11.79	81.33	6.88
6	15.23	23.98	60.79

Fig. 4. TEM and HAADF-STEM (insert figure) images of the reduced catalysts 10Ni10MgAl(one-pot) (left) and TEM image with EDX of reduced 10Ni5Mg5MgAl(impregnation) (right).

Fig. 5. TPR spectra of the catalysts: 1 - 5Ni5MgA-op, 2 - 10Ni10MgA-op, 3 - 10Ni5Mg5MgA-im.

of Ni metal particles as compared with the impregnated catalyst 10Ni5Mg5MgA-im in accordance with TEM data (Fig. 4).

3.3 Activity of the catalysts in methane dry reforming

The catalysts activated in the hydrogen feed at 650 °C were tested in methane dry reforming (MDR), at increasing, and then at decreasing temperature in order to evaluate the catalyst stability. Data on methane and CO₂ conversion, and the H₂/CO ratio are presented in Figs. 6-8 and Table 3. The values of reactant conversion are higher for the 5Ni5MgA-op and 10Ni10MgAl-op catalysts prepared using the one-pot method as compared with 10Ni5Mg5MgA-im (Table 3). For the one-pot catalysts, methane and CO₂ conversion only slightly rises at increasing nickel concentration up to 10 wt%. For both catalysts, methane and CO₂ conversions are equal at 750 °C while at lower temperatures conversion of CO₂ is larger due to the impact

Fig. 6. CH₄ and CO₂ conversion, H₂/CO during successive increasing and decreasing temperature in the range of 650-750 °C. The catalyst 5Ni5MgA-op (A), 10Ni10MgAl-op (B) and 10Ni(5Mg(5Mg-op))-im (C). The feed 15v.% CH₄+15v.%CO₂, He balance, contact time 0.015 s.

Table 3. Methane conversion at increasing and decreasing temperature.

Catalyst	Methane conversion, % at temperature, °C				
	650	700	750	700	650
5Ni5MgA-op	45	57	64	52	40
10Ni10MgA-op	47	58	64	54	42
10Ni5Mg5MgA-im	0	14	32	24	16

of the RWGS reaction. The H_2/CO ratio is equal to $\sim 0.72\text{--}0.8$ depending on the temperature (Figs. 6 A, B), which agrees with literature data [2, 15, 23]. Only a minor decrease in the reactant conversions during thermal cycling shows that stability of the one-pot catalysts is high.

In the case of the $10\text{Ni}5\text{Mg}5\text{MgA-im}$ catalyst prepared by impregnation, the methane and CO_2 conversions are low in the whole temperature range (Fig. 6 C). The absence of initial activity at 650°C might be caused by severe coking of the large metallic nickel particles formed on the catalyst surface in the course of reduction at 650°C . Indeed, Ni metal particles of up to $20\text{--}30\text{ nm}$ and their aggregates are clearly seen in the TEM image of the reduced $10\text{Ni}5\text{Mg}5\text{MgA-im}$ catalyst (Fig. 4). At temperatures above 650°C , the reduction of the nickel species strongly interacting with the support could occur under the reaction conditions and the catalyst shows some activity. Moreover, at higher temperatures the increase of the reactivity of carbonates coordinated to Mg cations located at the Ni particle/support interface is expected to provide a stable performance of these catalysts in methane dry reforming.

Thus, testing of the catalysts in MDR reveals the high activity and stability of the catalysts prepared by the one-pot EISA method due to the stabilization of Ni-metal particles of $2\text{--}12\text{ nm}$ in the $\text{Mg-Al}_2\text{O}_3$ of a mesoporous structure.

4 Conclusions

The ordered mesoporous Mg- and Ni-Mg-alumina samples of general formula $\text{xwt}\%\text{Mg-Al}_2\text{O}_3$ and $\text{ywt}\%\text{Ni-x wt}\%\text{Mg-Al}_2\text{O}_3$ ($x, y = 5, 10\%$ wt) have been synthesized by the one-pot evaporation induced self-assembly (EISA) method. The study of the textural and structural properties of the prepared samples using N_2 adsorption-desorption analysis, BET, XRD, TEM with EDX, HAADF-STEM, and H_2 -TPR have shown that the samples calcined at 700°C had an ordered mesoporous structure with the SSA of $170\text{--}250\text{ m}^2/\text{g}$, pore volume of $0.5\text{--}0.64\text{ cm}^3/\text{g}$ and narrow distribution of the pore size (mean $12\text{--}16\text{ nm}$). For the catalysts prepared by the one-pot EISA method, the size of the metal Ni particles was in the range of $3\text{--}12\text{ nm}$ and was conditioned by their confinement in the mesopores and the interaction with MgO and Al_2O_3 . Testing in methane dry reforming in the $15\text{v}\%\text{CH}_4 + 15\text{v}\%\text{CO}_2$ feed, with He balance, at $650\text{--}750^\circ\text{C}$ and the contact time of 0.015 s has shown a higher activity and stability of the ordered mesoporous $10\text{w}\%\text{Ni-10w}\%\text{Mg-Al}_2\text{O}_3$ catalysts prepared by the one-pot method as compared with the catalyst of

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