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Ni-Mg-Al solid basic layered double oxide catalysts prepared using surfactant-assisted coprecipitation method for CO₂ reforming of CH₄

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ABSTRACT

Ni-Mg-Al solid basic catalysts for CO₂ reforming of CH₄ were prepared using a surfactant-assisted coprecipitation method. The preferred orientations of the surfactants on the Ni(111) and Ni(200) crystal planes were investigated. The catalytic performance of the surfactant-modified catalysts was tested at 800 °C. The cetyltrimethylammonium bromide (CTAB)-modified catalyst (CB-LDO; LDO = layered double oxide) was further studied at various reaction temperatures. All the catalysts were characterized using Fourier-transform infrared spectroscopy, X-ray diffraction, temperature-programmed reduction, X-ray photoelectron spectroscopy, high-resolution transmission electron microscopy, and temperature-programmed oxidation. The results show that growth of the Ni(200) plane is promoted by tetrapropylammonium hydroxide and restrained by P123, PVP, and CTAB. The crystallinity degree of Ni(200) plays a key role in the activation of CH₄. The CB-LDO catalysts retain high activities and stabilities, because of the crystal phase transformation at high temperature during the reaction; this leads to the formation of spinel NiAl₂O₄ and exposure of the Ni(200) crystal plane.

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1. Introduction

The chief sources of CH₄ are natural gas, coal-bed gas, shale gas, and biogas. CO₂ is the main emission in the conversion and use of fossil fuels, and is also the major component of steel blast-furnace gas, converter gas, and furnace gas. There are large natural reserves of CH₄, and CO₂ is an inevitable product of fossil fuel use. CO₂ reforming of CH₄ (CO₂ + CH₄ → 2CO + 2H₂, ΔH_{298K}^o = 247 kJ/mol) is a potential efficient process for the preparation of synthesis gas (syngas), which is the most important step in CH₄ comprehensive use and CO₂ emission re-

duction. Recently, research on the development of catalysts for CH₄-CO₂ reforming has focused on identifying catalysts with higher activities and better stabilities for industrial applications. The transition elements in group VIII and noble metals such as Ru, Rh, Pt, and Ir are the most common active components used for catalytic reforming of CH₄ with CO₂. Although noble metal catalysts have high activities and are less sensitive to carbon deposition, their industrial applications are restricted by their high costs. Ni-based catalysts have been identified as promising catalysts for CO₂ reforming of CH₄, because of their high catalytic activities and low costs [1].

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Ni-Mg-Al-LDHs (LDH: layered double hydroxide) are a series of supramolecular materials formed by anion-cation intercalation assembly. Calcination of these materials results in the formation of solid basic layered double oxide (LDO) catalysts that exhibit excellent catalytic performances in CO₂ reforming of CH₄, because of their mesoporous structures. Xu et al. [2] used the surfactant (EO)₂₀(PO)₇₀(EO)₂₀ triblock copolymer (P123) as a soft template for evaporation-induced self-assembly to prepare a Ni-Mg-Al(O) catalyst with a mesoporous structure for CO₂ reforming of CH₄ at 700 °C [GHSV = 15000 mL/(h·g_{cat}), V(CH₄)/V(CO₂) = 1/1]. The catalyst was highly active and CH₄ conversion remained at 80% after reaction for 100 h. Zhang et al. [3] carried out dry reforming of CH₄ over a Ni-Mg-Al-LDHs catalyst. The catalyst was not deactivated after 160 h. In our previous work [4], we showed that Ni-Mg-Al-LDO catalysts derived from Ni-Mg-Al hydrotalcite had catalytic stability over a period of 2000 h on stream at GHSV = 8000 mL/(h·g_{cat}) and V(CH₄)/V(CO₂) = 1/1. The conversions of CH₄ and CO₂ remained over 95% after reaction for 2000 h.

The morphology, particle size, and some properties of hydrotalcite can be modified using surfactants [5]; this has the following advantages. (1) It overcomes the drawbacks caused by metal particle aggregation caused by high local concentrations when a precipitating agent is added to a solution. (2) It can also significantly improve metal dispersion and optimize the textural properties of the catalyst [6]. (3) Regulation of the intrinsic kinetics [7,8] and mitigation of carbon deposition [9] can be achieved by controlling the crystal planes exposed and preparing structures with surface defects. In this study, we prepared Ni-Mg-Al-LDO catalysts using a surfactant-assisted coprecipitation method, and evaluated their catalytic performances in CH₄ reforming of CO₂. The microscopic effects of surfactants on the Ni-Mg-Al hydrotalcite precursors and on the crystal structure, physicochemical properties, and exposure of different crystal planes of the Ni complex oxide were examined. The relationship between catalyst structure and its catalytic properties was explored.

2. Experimental

2.1. Catalyst preparation

Ni-Mg-Al solid basic catalysts were prepared using a surfactant-assisted coprecipitation method. A certain amount of Na₂CO₃ was dissolved into 100 mL deionized water, a surfactant was dissolved into another 50 mL deionized water, then added these two solutions into four flask respectively. A nitrate solution [120 mL, $n(\text{Ni} + \text{Mg})/n(\text{Al}) = 3$] was added dropwise to aqueous solutions of Na₂CO₃ ($n(\text{CO}_3^{2-})/n(\text{M}^{n+}) = 2/3$) containing either tetrapropylammonium hydroxide (TPAOH), P123, poly(vinylpyrrolidone) (PVP), cetyltrimethylammonium bromide (CTAB), or no surfactant, at 60 °C. Coprecipitation was performed under constant agitation at 60 °C; the pH was kept at 9.15 by adding 1 mol/L NaOH solution. The resulting suspension was stirred vigorously at 60 °C for 3 h. The final slurry mixture was transferred to a Teflon bottle and crystallized at 80 °C for 24 h. After aging, the precipitate, which was light

green, was removed from the supernatant and rinsed several times with deionized water until the pH was 7. The aged slurry was removed by filtration and dried in an oven at 80 °C overnight. A light-green solid was obtained after calcination of the final filter cake by slowly increasing the temperature (5 °C/min ramping rate) to 700 °C and maintaining the final temperature for 6 h. It is stressed that the mass fraction of NiO in the catalyst was controlled to 10%. The catalysts are denoted by TH-LDO, P3-LDO, PP-LDO, CB-LDO, and LDO.

2.2. Catalyst characterization

The functional groups of the catalyst precursor were identified by Fourier-transform infrared (FT-IR) spectroscopy (Bruker Vertex 70) using KBr pellets in the range 4000–400 cm⁻¹ at a resolution of 4 cm⁻¹.

The catalyst textures were investigated using the standard BET and BJH methods to calculate the specific surface areas and pore size distributions, using a Micromeritics ASAP 2020 system.

The crystalline phases of the catalysts were identified by X-ray diffraction (XRD), using a DX-2700 X-ray powder diffractometer with Cu K α radiation ($\lambda = 1.5405 \text{ \AA}$, 40 kV, 30 mA) in steps of 0.01° at a scanning rate of 8°/min from 5° to 85° under atmospheric pressure. The grain size of the catalysts were obtained using Scherrer's equation.

The dispersed state and morphology of the active metal were probed using high-resolution transmission electron microscopy (HRTEM; FEITECNAI G²F-20).

The active Ni valence states and electron binding energies (E_b) of the catalysts were studied by X-ray photoelectron spectroscopy (XPS, Thermo Fisher), using an Escalab 250 scanning microprobe instrument with Al K α radiation (30 kV, $h\nu = 1486.6 \text{ eV}$) in steps of 0.1 eV under ultrahigh vacuum ($2.0 \times 10^{-7} \text{ Pa}$), calibrated internally using the carbon deposit C 1s ($E_b = 284.6 \text{ eV}$). Background was subtracted using Shirley method.

The reductive properties of the catalysts were investigated by temperature-programmed reduction (TPR), using a TP-5000 (Xianquan China) instrument equipped with a thermal conductivity detector to establish the appropriate reduction temperature or measure the hydrogen consumption. The tests were performed using a quartz reactor containing the catalyst (50 mg) in 5% H₂ (balanced with N₂ 20 mL/min) and a heating rate of 10 °C/min, from room temperature to 900 °C.

The oxidation properties of carbon deposited on the used catalysts were investigated by temperature-programmed oxidation-mass spectrometry (O₂-TPO-MS), using a QIC-20 analytical instrument (HIDEN). The used catalyst (100 mg) was pretreated at 150 °C for 30 min in a He atmosphere, cooled to 50 °C, and then the atmosphere was switched to 5% O₂ (20 mL/min, Ar balance). The temperature was increased linearly to 900 °C at 10 °C/min. CO₂ ($m/z = 44$) in the effluent was detected using a mass spectrometer (QIC-20, HIDEN) and recorded as a function of temperature, which can determine the type of carbon species. The amount of carbon deposition of used catalysts was calculated by oxidation of the charcoal activated power as the standard.

2.3. Catalyst evaluation

The catalytic performances were evaluated using a fixed-bed quartz reactor of inner diameter 8 mm under atmospheric pressure. The catalyst (0.30 g, 40–60 mesh), diluted with quartz sand (1.70 g), was loaded into the reactor. A thermocouple was placed in the catalyst bed to monitor the reaction temperature. Prior to the reactions, the catalysts were reduced at 800 °C for 2 h in a flow of mixed gases [$V(\text{H}_2)/V(\text{N}_2) = 1:1$]. The molar ratio of CH_4 to CO_2 was 1:1 at a GHSV of 60000 $\text{mL}/(\text{h}\cdot\text{g}_{\text{cat}})$. The product gas was analyzed using a gas chromatograph (Haixin GC-950) on packed column (TDX-01 type, Ar as carrier gas) equipped with a thermal conductivity detector after passing a cold trap.

3. Results and discussion

3.1. Catalytic performance

The stability of the LDO catalyst prepared using coprecipitation without surfactant assistance in our previous work [4] was investigated at GHSV = 8000 $\text{mL}/(\text{h}\cdot\text{g}_{\text{cat}})$ [$V(\text{CH}_4)/V(\text{CO}_2) = 1:1$] at 800 °C. The conversions of CH_4 and CO_2 were stable, over 95%, after reaction for 2000 h. In this work, the GHSV was increased to 60000 $\text{mL}/(\text{h}\cdot\text{g}_{\text{cat}})$ ($\text{CH}_4/\text{CO}_2 = 1:1$) to accelerate catalyst deactivation, thereby shortening the evaluation time and increasing the catalyst screening speed. The catalytic activities with time on stream are shown in Fig. 1. The results show that the surfactant significantly affects the catalytic activity. A comparison with the LDO catalyst without a surfactant shows that TPAOH clearly promotes the reaction, and the initial conversions of CH_4 and CO_2 over TH-LDO are above 95%. However, additions of P123, PVP, and CTAB surfactants have an inhibitory effect. It is worth noting that the initial CH_4 conversion over PP-LDO is only 18%, and that over CB-LDO is nearly zero. However, the CH_4 and CO_2 conversions over CB-LDO quickly reach their peaks in a few hours. These results show that the initial activities of the catalysts synthesized by different surfactant-assisted methods vary greatly, which suggests that the

surfactants significantly affect the structures and surface states of the fresh catalysts.

3.2. Analysis of catalytic activity

The XRD patterns of the uncalcined catalysts are shown in Fig. 2(a). It can be seen that no peaks for oxide or hydroxide crystalline phases are present, only the characteristic LDH reflections of the (003), (006), (009), (015), (018), (110), and (113) planes, indicating that the precursors are pure LDH phases. In the precursor patterns, the sharp characteristic peaks of the (003) plane of the hydrotalcite-like LDH phase, which determines the interlamellar spacing, are strong [10] and symmetric. In addition, the (110) and (113) crystal plane diffraction peaks are clearly distinguishable. These results suggest that the synthetic Ni-Mg-Al-LDHs are hexagonal structures with high crystallinities, and confirm that the surfactant-assisted coprecipitation method gives perfect Ni-Mg-Al-LDHs. The lattice parameters, including a [$a = 2d_{(003)}$] and c [$c = d_{(003)} + 2d_{(006)} + 3d_{(009)}$], calculated using the Scherrer equation, are listed in Table 1. The value of a is the average semi-diameter of the metal cations in the interlayer structure, and c is closely related to the distance, charge density, anion size, and amount of water molecules in the interlayer structure [11]. The data show that adding TPAOH, PVP, or CTAB decreased c , indicating an increase in the positive charge density in the laminates and enhancement of the coulombic forces of laminates and anions between the layers. However, adding P123 increased c , which indicates a decrease in positive charge density in the laminates and a decrease in the coulombic forces of laminates and anions between layers. The reason is that TPAOH and CTAB are quaternary ammonium salts, and the N atom is connected to a carbonyl in PVP. The N atoms in these three compounds are therefore electron deficient, which increases the coulombic forces of laminates and anions between layers. P123 is electrically neutral, with no electron-deficient center and lone pair electrons on the oxygen, which leads to an electron cloud of high density; this decreases the density of positive charges on laminates and the coulombic forces of lam-

Fig. 1. CH_4 (a) and CO_2 (b) conversions over catalysts with time on stream at 800 °C. Reaction conditions: $\text{CH}_4/\text{CO}_2 = 1/1$, $p = 0.1$ MPa, GHSV = 60000 $\text{mL}/(\text{h}\cdot\text{g}_{\text{cat}})$.

Fig. 2. XRD patterns (a) and FT-IR spectra (b) of catalysts before calcination; XRD patterns of catalysts after calcination and reduction (c, d). (1) TH-LDO; (2) LDO; (3) P3-LDO; (4) PP-LDO; (5) CB-LDO.

inates and anions between layers. These results, combined with the catalytic performances shown in Fig. 1, show that electro-positive surfactants enhance the coulombic forces of laminates and anions between layers. This is the main reason for the clear promotion of catalytic activity.

The FT-IR spectra of the LDH precursors are presented in Fig. 2(b). All the samples show broad bands at 3543 cm^{-1} , from the stretching mode of structural -OH groups in the metal hydroxide layer. A small shoulder at 2925 cm^{-1} is ascribed to a second type of -OH stretching vibration, arising from interlayer hydrogen bonding with carbonate groups. A weak sharp band

at 1120 cm^{-1} shows the presence of C-N single bonds [12]. The strong band at 1370 cm^{-1} and weak band at 858 cm^{-1} are attributed to the stretching vibration and out-of-plane bending vibration of CO_3^{2-} , respectively. The weak band at 1637 cm^{-1} is ascribed to the bending vibration [deformation mode of H-O-H ($\delta\text{H-O-H}$)] of interlayer water molecules in the LDH. The bands in the range 500–750 cm^{-1} are typical of the frameworks of LDH materials, and indicate M-O-M stretching ($\text{M} = \text{Mg, Ni, and Al}$) [13]; this further confirms that the precursors are ordered LDHs.

The XRD patterns of the Ni-Mg-Al-LDO catalysts after calcination and reduction are shown in Fig. 2(c). All the catalysts exhibit the characteristic peaks of Mg(Ni, Al)O periclase at $2\theta = 36.4^\circ, 43.4^\circ, 62.9^\circ$, and 79.2° [14]. The peaks observed at $2\theta = 44.5^\circ, 51.8^\circ$, and 76.3° are assigned to the Ni(111) , (200) , and (220) planes, respectively. It can be clearly seen from Fig. 2(c) that the crystallinities indicated by the Ni(111) and Ni(200) reflections vary, and the intensities of the Ni(200) reflections increase significantly in the order CB-LDO, PP-LDO, P3-LDO, LDO, and TH-LDO. To avoid measurement errors caused by

Table 1
Structure of different precursors.

Sample	$d_{(003)}$ (nm)	$d_{(006)}$ (nm)	$d_{(009)}$ (nm)	$d_{(110)}$ (nm)	a (nm)	c (nm)
TH-LDH	7.715	3.860	2.582	1.525	3.050	23.181
LDH	7.715	3.867	2.598	1.526	3.052	23.243
P3-LDH	7.776	3.880	2.589	1.526	3.052	23.303
PP-LDH	7.716	3.870	2.582	1.526	3.052	23.202
CB-LDH	7.687	3.857	2.587	1.523	3.052	23.162

different frequencies, the shoulder reflection of the Ni(111) plane at $2\theta = 44.5^\circ$ is used as the primary standard for the measurements, and the relative intensity of the Ni(200) reflection is set at $I_{\text{Ni}(200)}/I_{\text{Ni}(111)}$. The values of $I_{\text{Ni}(200)}$ and $I_{\text{Ni}(111)}$ are estimated, using the Scherrer equation, from the full-widths at half-maximum of the peaks at $2\theta = 51.8^\circ$ and 44.5° , respectively. It can be seen that the order of the calculated $I_{\text{Ni}(200)}/I_{\text{Ni}(111)}$ values of the catalysts is TH-LDO (27.7%) > LDO (25.4%) > P3-LDO (22.0%) > PP-LDO (14.3%) > CB-LDO (11.1%); this agrees with the initial conversions of CH_4 and CO_2 in Fig. 1. These results indicate that the Ni(200) plane significantly affects the catalytic activity. The degree of exposure of the Ni(200) crystal plane differs among the catalysts, and can be traced to the adsorptive capacity of the surfactant on the crystal plane. The surfactants are directionally adsorbed on different planes, and this affects the surface free energies of crystals and the crystal plane growth rate, resulting in modification of the metal particle size and morphology [15].

Figure 3 shows the HRTEM images of catalysts after calcination and reduction. The d values of the two main exposed crystal planes are 0.203 and 0.176 nm, respectively. A combination of these results and the corresponding fast Fourier-transform images enables identification of Ni(111) and Ni(200) [16,17]. However, the absence of Ni(200) in the CB-LDO sample (Fig. 3(e)) indicates that the crystalline form was transformed and grew a second time, but the growth of the crystal plane protected by a surfactant was restrained.

The crystalline structure of Ni is face-centered cubic (fcc). Because of the symmetry features of the fcc structure, the lat-

eral faces can alternate between the Ni(100) and Ni(111) crystal planes. Ni(200) is the second-order diffraction of Ni(100) in the cell structure, (200) is the interference index, and (100) is the crystal plane index; their contributions to the space lattice are the same, despite their different definitions. Ni(200) in the XRD patterns is therefore equal to Ni(100) in the space lattice. The high energy of the average band d is not beneficial to CH_x decomposition, so Ni(100) could decrease the activation energy barrier and promote the decomposition of CH_x [18]. Ni(100) [i.e., Ni(200)] rather than Ni(111) is the main adsorption surface when CH_4 decomposes [19]; this could explain the relationship between the relative intensity of Ni(200) and the activity.

The H_2 -TPR profiles of the catalysts after calcination are shown in Fig. 4. The peak temperatures range from 370 to 866 °C, suggesting various types of interaction between NiO species and the mesoporous skeleton of the Ni-Mg-Al-LDO sample. According to literature reports, the reduction peaks from 370 to 450 °C can be attributed to the reduction of pure NiO [20,21], and the reduction peaks from 500 to 800 °C are associated with weak interactions between Ni^{2+} and Al_2O_3 or MgO [22,23]. The peak above 800 °C is attributed to the reduction of Ni^{2+} in a Ni-Mg solid solution or Ni-Al spinel [24,25]. The order of the high reduction peak temperatures, i.e., TH-LDO (866 °C) > LDO (840 °C) > P3-LDO (817 °C) > PP-LDO (787 °C) > CB-LDO (702 °C), is in accordance with the order of the initial activities. This indicates that strong interactions between Ni particles and the support provide the main catalytically active sites. It has been reported that strong metal-support interactions (SMSIs) form

Fig. 3. HRTEM micrographs of catalysts after calcination and reduction. (a) TH-LDO; (b) LDO; (c) P3-LDO; (d) PP-LDO; (e) CB-LDO.

Fig. 4. H_2 -TPR profiles of catalysts after calcination.

connections between Ni particles and the support that are more compact and harder to reduce. SMSIs could also suppress sintering of Ni particles and carbon deposition on Ni, and these effects help to achieve high catalytic activity and stability [26–28].

The XPS spectra of the catalysts after calcination and reduction are shown in Fig. 5. The binding energy of the peak at 852.5 eV is attributed to Ni^0 [29], which is in accordance with the weak interaction between Ni^{2+} and Al_2O_3 or MgO in the H_2 -TPR results. The binding energies of the peaks at 855.4 and 857.3 eV are attributed to Ni^{2+} and Ni^{3+} , with a satellite peak from $Ni^{2+} 2p_{3/2}$ at 861.2 eV [30,31]. The presence of high binding energies of Ni^{2+} confirm the presence of Ni-Al spinel [32]. Ni^0 , Ni^{2+} , and Ni^{3+} species are present on the catalyst surfaces after calcination and reduction; this is in accordance with the

TPR results, which show that Ni species are not totally reduced at 800 °C. No regular relationships are seen among the peak areas of Ni^0 , Ni^{2+} , and Ni^{3+} in Figs. 4 and 5; this may be because of unavoidable oxidation of the samples before XPS was performed. However, it has been reported that Ni^{x+} ($x = 0, 2, 3$) species may collaboratively promote the reaction [33].

TEM micrographs and histograms of the Ni particle size distribution on the catalysts after calcination and reduction are shown in Fig. 6. The particle sizes are smaller than those calculated from the XRD (Table 2); this is because no correction was applied for widening of the XRD peaks. The most probable particle sizes of TH-LDO, LDO, and P3-LDO are around 10 nm, and the distribution widths are slightly different. The most probable particle sizes of PP-LDO and CB-LDO are 8 and 6 nm, respectively. The distribution width of PP-LDO is the narrowest. The smaller Ni particle size and narrowest distribution width are probably caused by the strong coordination of PVP with metal ions and the compressibility of the c value of hydrotalcite. Similar phenomena for CB-LDO are caused solely by the compressibility of the c value of hydrotalcite (Table 1). The TPR results also support the conclusion that PP-LDO and CB-LDO have the smallest particle sizes (Fig. 4). The reduction peak temperatures of both samples are less than 800 °C, indicating that the reduction peaks could not be entirely attributed to the reduction of Ni^{2+} in a Ni-Mg solid solution or Ni-Al spinel [24,25]; they could be ascribed to the reduction of highly dispersed NiO particles with weak interactions with Al_2O_3 or MgO [22,23]. A combination of these results and the catalytic performances suggests that the NiO particles mentioned above make no contribution to the initial catalytic activity.

Figure 7 shows the N_2 adsorption-desorption isotherms and pore size distributions for the TH-LDO, LDO, and CB-LDO cata-

Fig. 5. XPS spectra of Ni $2p_{3/2}$ band of catalysts after calcination and reduction. (a) TH-LDO; (b) LDO; (c) P3-LDO; (d) PP-LDO; (e) CB-LDO.

Fig. 6. TEM micrographs and histograms of Ni particle size distributions on catalysts after calcination and reduction; selected area diffraction pattern of the LDO catalyst. (a) TH-LDO; (b) LDO; (c) P3-LDO; (d) PP-LDO; (e) CB-LDO.

lyst samples after calcination. The TH-LDO, LDO, and CB-LDO catalysts have typical type IV isotherms with a hysteresis loop, and show a phase step at $p/p_0 = 0.5$ – 0.6 , 0.7 – 0.8 , and 0.8 – 0.9 , respectively (Fig. 7(a)). The results show that all the samples are mesoporous materials. The TH-LDO and LDO catalysts have typical type IV isotherms with an H1 hysteresis loop. These N_2 adsorption-desorption isotherms indicate that TH-LDO and LDO have highly ordered porous structures, and the mean pore diameters of the catalysts show highly localized distributions (Fig. 7(b)). The typical type IV isotherm with an H3 hysteresis loop of CB-LDO shows that it has large, diffuse slit-shaped pores, caused by accumulation of plate-like particles, causing aggregation or agglomeration of particles in solid CB-LDO [34,35]. Table 3 shows the N_2 adsorption results for the TH-LDO, LDO, and CB-LDO catalysts. The result shows that

there are significant differences among the textural properties of the catalysts before reaction, but after reaction, the textural properties of the catalysts are similar. These results are in agreement with those from the catalytic performance tests, i.e., the initial activities of all the catalysts are different, but after reaction, all the catalytic activities are similar. A comparison of the surface areas [TH-LDO ($251 \text{ m}^2/\text{g}$) > LDO ($182 \text{ m}^2/\text{g}$) > CB-LDO ($106 \text{ m}^2/\text{g}$)] and pore volumes indicates that a higher surface area and larger pore volume improve the CH_4 - CO_2 reforming reaction, and surfactants significantly influence the textural properties of the catalysts.

Table 2
Physicochemical properties of catalysts.

Catalyst	Ni ⁰ crystal size ^a (nm)		Average carbon deposition rate of used sample ^b ($\text{mg}_c/(\text{h} \cdot \text{g}_{\text{cat}})$)
	Reduced	Used	
TH-LDO	14.5	14.0 (800 °C)	2.072
LDO	13.5	13.0 (800 °C)	4.329
P3-LDO	14.5	13.0 (800 °C)	5.461
PP-LDO	15.0	13.0 (800 °C)	1.348
CB-LDO	unmeasured	16.0 (800 °C)	1.679
		10.5 (900 °C)	0.483
		12.5 (1000 °C)	0.148

^a Calculated from XRD data of Ni(111) and Ni(200) with Scherrer equation.

^b Calculated from the integral area of O_2 -TPO-MS curve line by using the software origin 8.0 (Charcoal activated power as the standard).

Fig. 7. N_2 adsorption-desorption isotherms (a) and pore size distributions (b) of catalysts after calcination.

Table 3

Textural properties of calcined and used (800 °C) catalysts.

Catalyst	BET surface area (m ² /g)		Pore size (nm)		Pore volume (cm ³ /g)	
	Calcined	Used	Calcined	Used	Calcined	Used
TH-LDO	251	140	8.11	10.43	0.58	0.40
LDO	182	145	8.79	10.15	0.41	0.37
CB-LDO	106	135	14.50	11.21	0.38	0.43

3.3. Evaluation of catalyst stability

The catalytic activities and stabilities of the Ni-Mg-Al-LDO catalysts are shown in Fig. 1. Experiments showed that the times on stream before CH₄ conversion decreased to 48% were 35 h for TH-LDO, 32 h for LDO, and 26 h for CB-LDO. CB-LDO showed an initial induction period of 4 h, during which no catalytic activity was detected. However, when the reaction time reached 10 h, the activity quickly increased to a maximum, and remained stable for 4 h, before deactivation. The results show that the deactivation times are different, but the deactivation rates are similar, for all the samples. This suggests that catalyst deactivation is mainly caused by external rather than intrinsic factors. To inhibit catalyst deactivation, it is necessary to investigate the real cause of the deactivation. The existence of an induction period for CB-LDO may be caused by encapsulation of fine particles of Ni species within the support, resulting in no active sites being available for CH₄ cracking. The Ni particle size distributions and the blurred images in Fig. 6(e) confirm that Ni species were encapsulated within the support. The short induction periods also demonstrate that the pseudo-matrix formed can be quickly destroyed and reconstructed with the aid of heat from ion migration during the sustained high-temperature reaction. The active Ni species are then exposed and the catalytic reaction proceeds (Fig. 8). The effect of reaction temperature on the catalytic performance of CB-LDO was further investigated, to confirm our deduction.

Figure 9(a–c) shows the results of evaluation of the catalytic activities and stabilities with time at 800, 900, and 1000 °C for CB-LDO. The results suggest that higher temperatures benefit CO₂ reforming of CH₄. However, the induction period cannot be eliminated, only shortened to a certain extent. Our preliminary deduction is that fine particles of Ni species were encapsulated within the support. A comparison of the XRD patterns of the reduced CB-LDO catalyst and the CB-LDO used at different temperatures (Fig. 9(d)) shows that there are no diffraction peaks for Ni⁰ or Ni(Mg)Al₂O₄ spinel from the reduced catalyst. In addition, no peak for crystalline Ni(Mg)Al₂O₄ spinel is detected in the catalyst used at 800 °C. However, Ni(111),

Ni(200), Ni(220), and Ni(Mg)Al₂O₄ spinel reflections [36,37] are detected for the catalysts used at 900 and 1000 °C, indicating that formation of Ni(Mg)Al₂O₄ spinel causes exposure of the Ni (200) crystal plane. The order of the relative intensities of the Ni (200) reflections in the used catalysts [CB-LDO (35.6%) 1000 °C > CB-LDO (32.2%) 900 °C > CB-LDO (30.5%) 800 °C] further supports the proposal that that catalytic activity is related to Ni(200) exposure. The Ni(Mg)Al₂O₄ spinel formed in the reforming reaction at high temperature clearly enables slow release of Ni encapsulated within the support, and exposure of the Ni(200) plane stabilizes the catalytic activity under high-temperature conditions.

The XRD results show that the main catalyst phase before reaction is NiO–MgO periclase with a cubic octahedral structure. According to the laws of thermodynamics, both the free energy and surface energy of a cubic octahedron are lower than those of a cube, therefore cubic octahedra have more stable states [38]. The study by Chen et al. [39] showed that spinel NiAl₂O₄ can significantly inhibit the formation of carbon deposits. In our experiments, the performance of the CB-LDO catalyst was better at 1000 °C than at 800 and 900 °C. The same conclusion can be drawn from the phenomenon mentioned above. Clearly, a higher temperature improves the catalytic activity and stability. Theoretically, a higher temperature can accelerate the sintering of active metal particles and the formation of carbon deposits. However, a higher temperature can also enable reconstruction of the catalyst phase, which is useful. The data in Table 2 show that the average particle sizes of CB-LDO at 900 and 1000 °C are significantly smaller than that at 800 °C. The conclusion that a higher temperature causes adverse changes therefore cannot be generalized.

To confirm the universality of the above conclusion, the best catalyst at 800 °C, i.e., TH-LDO, was evaluated at 900 °C (Fig. 10). The results show that the initial CH₄ conversion is almost the same at both temperatures. However, the catalytic activity at 900 °C decreases by about 10% compared with that at 800 °C at intermediate reaction times. Thereafter, the deactivation rate of TH-LDO at 900 °C is slower than that at 800 °C. The deactivation rate of TH-LDO is different from that of the CB-LDO catalyst, but they are both deactivated slowly at higher temperatures.

3.4. Analysis of catalyst deactivation

In CH₄–CO₂ reforming, the deactivation of Ni-based catalysts is mainly caused by sintering of active metal particles, and coke formation on the catalyst surface [40–42]. Sintering promotes aggregation of Ni particles and increases their size. In this

Fig. 8. Schematic diagram of release of active sites on Ni catalyst during CH₄–CO₂ reforming.

Fig. 9. CH₄ (a) and CO₂ (b) conversions and H₂/CO product ratios (c) using CB-LDO catalyst with time on stream at various temperatures; (d) XRD patterns of CB-LDO catalyst. Reaction conditions: CH₄/CO₂ = 1/1, p = 0.1 MPa, GHSV = 60000 mL/(h·g_{cat}).

study, the sizes of the Ni particles before and after reaction were almost the same, indicating that deactivation is mainly caused by carbon deposition, not catalyst sintering. The approximate deactivation rates of catalysts modified with different surfactants suggest that the growth rate of carbon deposits on the catalysts is determined by the properties of the coke and is not influenced by the catalyst characteristics. Coke formation

should therefore be suppressed by the initial formation of coke.

The main source of carbon deposition in the CH₄-CO₂ reforming system is shown in reactions (1) and (2) [43–45]. It has been reported that there are three types of carbon deposited on catalysts after reaction, and they are classified based on the peak temperatures of the TPO-MS curves [25,46,47]: (1) atomic carbon (C_α, $T < 250$ °C), (2) amorphous carbon (C_β, 300 °C $< T < 500$ °C), and (3) graphitic carbon (C_γ, 600 °C $< T < 700$ °C). C_α and C_β are oxidized above 300 °C and transformed into syngas in the reaction system. In contrast, C_γ is oxidized above 700 °C, and it is hard to transform it into syngas [46,48,49]. The morphology of the carbon deposit is related to the graphitization degree, and the oxidizing temperature increases with increasing carbon crystallinity [49,50].

The O₂-TPO-MS profiles of the catalysts after reaction at 800 °C are presented in Fig. 11(a). CO₂ signals are observed from 330 to 750 °C. It shows from Fig. 11(a) and Table 2 that the average carbon deposition rates of TH-LDO, LDO, and P3-LDO are high, especially for C_γ, and the rates for PP-LDO and CB-LDO are low. These results are in accordance with the order of the most probable pore diameters of the Ni particles, obtained using TEM, and this also proves that carbon is more easily deposited on larger Ni particles [51,52]. In general, small Ni⁰ particles have high catalytic activity and can suppress carbon deposition,

Fig. 10. CH₄ conversions over LDO catalyst with time on stream at various temperatures. Reaction conditions: CH₄/CO₂ = 1/1, p = 0.1 MPa, GHSV = 60000 mL/(h·g_{cat}).

Fig. 11. O₂-TPO-MS (a) and XRD patterns (b), and TEM micrographs (c, d) of catalysts at 800 °C after stability tests.

and large Ni⁰ particles have low catalytic activity and carbon deposition is higher. The Ni particles in PP-LDO and CB-LDO are the smallest, and the average carbon deposition rates and initial activities of these catalysts are both very low. This indicates that the crystal orientation is also important in the catalytic activity.

The XRD patterns of the catalysts after reaction at 800 °C are shown in Fig. 11(b). There is a specific diffraction peak at $2\theta = 26^\circ$, which is attributable to graphitic carbon. Active metal encapsulation by carbon is observed in Fig. 11(c–d). The crystalline interplanar spacing of carbon is 0.336 nm, measured from Fig. 11(d), which is similar to the value of 0.334 nm reported in the literature [53]. The clear lattice lines imply a high graphitization level of carbon, in accordance with the TPO-MS results.

The O₂-TPO-MS profiles of CB-LDO after reaction at various temperatures are presented in Fig. 12(a). The amount of gra-

Fig. 12. (a) O₂-TPO-MS profiles of CB-LDO after stability tests at various temperatures; (b) TEM micrographs of CB-LDO catalyst after reaction at 1000 °C.

phitic carbon increases with increasing reaction temperature. This is not specifically caused by the different reaction temperatures, because the reaction times for the three samples are also different: (1) 34 h for the sample reacted at 800 °C; (2) 100 h for the sample reacted at 900 °C; and (3) 456 h for the sample reacted at 1000 °C. Their average carbon deposition rates are listed in Table 2. The average carbon deposition rate of the sample at 800 °C was the highest, 1.679 mg_c/(h·g_{cat}). The most probable particle size (13 nm) is close to the value (12.5 nm) calculated from the XRD patterns and is larger than the particle size after reduction (6 nm). This is the result of restructuring of catalyst species during the reaction. Ni encapsulation is also observed in the TEM micrograph; the lattice spacing is 0.213 nm, which is different from the spacing of the graphitic carbon layers (0.334 nm) and similar to the lattice spacing (0.211 nm) of MgO(200) (JCPDS 450946), obtained from the XRD pattern. This suggests that Ni is encapsulated by MgO and is released during the reaction at higher temperature, which exposes active sites on Ni(200). The catalyst therefore shows excellent stability and activity in the reaction at higher temperature.

4. Conclusions

In summary, the thickness, electron density, and laminar spacing of Ni-Mg-Al-LDHs precursors can be effectively regulated using a surfactant-assisted coprecipitation method. The physicochemical properties, microtextures, and crystal orientations of the fresh Ni-Mg-Al-LDO catalysts are affected by the surfactant. Different surfactants have different charge properties and various coordination abilities toward metal ions, and these influence the metal particle size and promote or restrain the growth of specific crystal planes. The catalytic performance depends not only on the Ni particle size, but is also affected by the relative degree of exposure of Ni(200). The reconstruction of catalyst species at high temperatures improves the catalytic activity, and this can be ascribed to controlled release of the Ni(200) crystal plane. This study demonstrates that carbon deposition is the main cause of deactivation of Ni-Mg-Al-LDO catalysts. Surfactants influence the initial generation of carbon to some extent. However, once carbon deposition starts, the carbon deposition rate is determined by the carbon type rather than the catalyst properties. The initial carbon deposition should therefore be suppressed, but the dynamic equilibrium point between carbon deposition and elimination needs to be established, and appropriate catalysts developed to solve the problem of carbon deposition.

References

- [1] Naomohan, Fu X J, Lei Y Q, Zhang H J, Su H Q. *Chin J Catal* (瑙莫汗, 付晓娟, 雷艳秋, 苏海全. 催化学报), 2014, 34: 379
- [2] Xu L L, Song H L, Chou L J. *Appl Catal B*, 2011, 108-109: 177
- [3] Zhang X Q, Wang N, Xu Y, Yin Y X, Shang S Y. *Catal Commun*, 2014, 45: 11
- [4] Shen C F. [MS Dissertation]. Tai yuan: Taiyuan Univ Technol (沈朝峰. [硕士研究生学位论文]. 太原: 太原理工大学), 2013
- [5] Forano C, Hibino T, Leroux F, Taviot-Guho C. *Developments in Clay Science*, 2006, 1: 1021
- [6] Ren S B, Wen H Z, Cao X Z, Wang Z C, Lei Z P, Pan C X, Kang S G, Shui H F. *Chin J Catal* (任世彪, 文宏志, 曹先中, 王知彩, 雷智平, 潘春秀, 康士刚, 水恒福. 催化学报), 2014, 35: 546
- [7] Xiang G L, Wang X. *Chin J Inorg Chem* (相国磊, 王训. 无机化学学报), 2011, 27: 2323
- [8] Li Y, Shen W J. *Sci Chin Chem*, 2012, 55: 2485
- [9] Hu Q H, Li X C, Yang A J, Yang C Y. *Chin J Catal* (胡全红, 黎先财, 杨爱军, 杨春燕. 催化学报), 2012, 33: 563
- [10] Rives V. *Mater Chem Phys*, 2002, 75: 19
- [11] Gao P, Li F, Zhao N, Wang H, Wei W, Sun Y H. *Acta Phys-Chim Sin* (高鹏, 李枫, 赵宁, 王慧, 魏伟, 孙予罕. 物理化学学报), 2014, DOI: 10.3866/PKU.WHXB201401252
- [12] Djebbari B, Gonzalez-Delacruz V M, Halliche D, Bachari K, Saadi A, Caballero A, Holgado J P, Cherifi O. *Reac Kinet Mech Catal*, 2014, 111: 259
- [13] Zaghoulane-Boudiaf H, Boutahala M, Arab L. *Chem Eng J*, 2012, 187: 142
- [14] Li D L, Atake I, Shishido T, Oumi Y, Sano T, Takehira, K. *J Catal*, 2007, 250: 299
- [15] Nam H S, Hwang N M, Yu B D, Yoon J K. *Phys Rev Lett*, 2002, 89: 275502
- [16] Shen X J, Yang J P, Liu Y, Luo Y S, Fu S Y. *New J Chem*, 2011, 35: 1403
- [17] Li P W, Wang N, Wang R M. *Eur J Inorg Chem*, 2010: 2261
- [18] Li J D, Croiset E, Ricardez-Sandoval L. *J Mol Catal A*, 2012, 365:

Graphical Abstract

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Ni-Mg-Al solid basic layered double oxide catalysts prepared using surfactant-assisted coprecipitation method for CO₂ reforming of CH₄

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Highly dispersed Ni particles were encapsulated by cetyltrimethylammonium bromide. The Ni(200) plane was slowly released by Ni(Mg)Al₂O₄ spinel formation, giving excellent catalytic performances at high temperatures for CO₂ reforming of CH₄.

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- [19] Wang S G, Cao D B, Li Y W, Wang J G, Jiao H J. *Surf Sci*, 2006, 600: 3226
- [20] Wang Q S, Ren W, Yuan X L, Mu R M, Song, Z L, Wang X L. *Int J Hydrogen Energy*, 2012, 37: 11488
- [21] Kumar P, Sun Y P, Idem R O. *Energy Fuels*, 2008, 22: 3575
- [22] Xiao H P, Liu Z C, Zhou X G, Zhu K K. *Catal Commun*, 2013, 34: 11
- [23] Bang Y J, Han S J, Yoo J K, Choi J H, Kang K H, Song J H, Seo J G, Jung J C, Song I K. *Int J Hydrogen Energy*, 2013, 38: 8751.
- [24] Dieuzeide M L, Iannibelli V, Jobbagy M, Amadeo N. *Int J Hydrogen Energy*, 2012, 37: 14926.
- [25] Du X J, Zhang D S, Shi L Y, Gao R H, Zhang J P. *Nanoscale*, 2013, 5: 2659.
- [26] Mora M, Jiménez-Sanchidrián C, Ruiz J R. *J Colloid Interf Sci*, 2006, 302: 568
- [27] Lucrédio A F, Jerkiewicz G, Assaf E M. *Appl Catal A*, 2007, 333: 90
- [28] Wang Z T, Shao X, Larcher A, Xie K, Dong D H, Li C Z. *Catal Today*, 2013, 216: 44
- [29] Kang K M, Kim H W, Shim I W, Kwak H Y. *Fuel Process Technol*, 2011, 92: 1236
- [30] Ning F Y, Shao M F, Zhang C L, Xu S M, Wei M, Duan X. *Nano Energy*, 2014, 7: 134
- [31] Hou J, Liu Z M, Lin G D, Zhang H B. *Int J Hydrogen Energy*, 2014, 39: 1315
- [32] Liu D P, Wang Y F, Shi D M, Jia X L, Wang X, Borgna A, Lau R, Yang Y H. *Int J Hydrogen Energy*, 2012, 37: 10135
- [33] Damyanova S, Pawelec B, Arishtiroya K, Fierro J L G. *Int J Hydrogen Energy*, 2012, 37: 15966
- [34] Salam M A, Sufian S, Murugesan T. *Mater Chem Phys*, 2013, 142: 213
- [35] Alvar E N, Rezaei M. *Scripta Mater*, 2009, 61: 212
- [36] Hadian N, Rezaei M, Mosayebi Z, Meshkani F. *J Nat Gas Chem*, 2012, 21: 200
- [37] Zhai X L, Ding S, Liu Z H, Jin Y, Cheng Y. *Int J Hydrogen Energy*, 2011, 36: 482
- [38] Bai Y, Long R, Wang C M, Xiong Y J. *J Univ Sci Technol Chin* (柏戡, 龙冉, 王成名, 熊宇杰. 中国科学技术大学学报), 2013, 43: 889
- [39] Chen Y G, Ren J. *Catal Lett*, 1994, 29: 39.
- [40] Liu C J, Ye J Y, Jiang J J, Pan Y X. *ChemCatChem*, 2011, 3: 529
- [41] Zhu J Q, Peng X X, Yao L, Tong D M, Hu C W. *Catal Sci Technol*, 2012, 2: 529
- [42] Wang N, Yu X P, Shen K, Chu W, Qian W Z. *Int J Hydrogen Energy*, 2013, 38: 9718
- [43] Eltejaei H, Reza Bozorgzadeh H, Towfighi J, Reza Omidkhan M, Rezaei M, Zanganeh R, Zamaniyan A, Zarrin Ghalam A. *Int J Hydrogen Energy*, 2012, 37: 4107
- [44] Koerts T, Van Santen R A. *J Chem Soc, Chem Commun*, 1991: 1281
- [45] Shi C K, Zhang P. *Appl Catal B*, 2012, 115-116: 190
- [46] Hao Z G, Zhu Q S, Jiang Z, Hou B L, Li H Z. *Fuel Process Technol*, 2009, 90: 113
- [47] Zhang Z L, Verykios X E. *Catal Today*, 1994, 21: 589
- [48] Zhang H, Li M, Xiao P, Liu D, Zou C J. *Chem Eng Technol*, 2013, 36: 1701.
- [49] Sun L Z, Tan Y S, Zhang Q D, Xie H J, Song F, Han Y Z. *Int J Hydrogen Energy*, 2013, 38: 1892
- [50] Long J W, Laskoski M, Keller T M, Pettigrew K A, Zimmerman T N, Qadri S B, Peterson G W. *Carbon*, 2010, 48: 501
- [51] Tang S, Ji L, Li J, Zeng H C, Tan K L, Li K. *J Catal*, 2000, 194: 424
- [52] Zhang J G, Wang H, Dalai Ajay K. *Appl Catal A*, 2008, 339: 121
- [53] Kroll V C H, Swaan, H M, Mirodatos C. *J Catal*, 1996, 161: 409

表面活性剂辅助共沉淀法制备Ni-Mg-Al固体碱催化剂用于CH₄-CO₂重整反应

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摘要: 采用表面活性剂辅助共沉淀法制备了Ni-Mg-Al固体碱催化剂并用于CH₄-CO₂重整反应, 探讨了表面活性剂对Ni(111), Ni(200)晶面的择优取向作用, 在800 °C下比较了不同表面活性剂制备的催化剂的催化性能, 详细考察了CTAB制备的催化剂CB-LDO在不同反应温度下的催化活性和稳定性. 采用红外光谱、X射线衍射、程序升温还原、X射线光电子能谱、高分辨透射电镜和程序升温氧化等表征手段分析了催化剂的活性、稳定性和失活原因. 结果表明, 四丙基氢氧化铵(TPAOH)促进Ni(200)的生长, 而聚氧乙烯-聚氧丙烯-聚氧乙烯(P123)、聚乙烯吡咯烷酮(PVP)和十六烷基三甲基溴化铵(CTAB)抑制Ni(200)晶面的生长; Ni(200)的结晶程度对CH₄的活化起到关键的作用, 催化剂CB-LDO在高温下反应会发生晶型的转化, Ni(200)晶面由于反应过程中生成NiAl₂O₄尖晶石而得到缓慢释放, 使催化剂的活性得以维持较高的水平.

关键词: 表面活性剂; 共沉淀法; 镍; 镁铝氧化物; 甲烷; 二氧化碳; 重整

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1. 前言

CH₄是天然气、煤层气、页岩气、沼气的成分,

在自然界中储量巨大; CO₂是化石能源转化与利用中最主要, 也是必然的排放物, 是炼钢高炉气、转炉气、窑炉的主要成分. 将CH₄和CO₂进行重整制取合成气(CO₂ +

$\text{CH}_4 \rightarrow 2\text{CO} + 2\text{H}_2$, $\Delta H_{298\text{K}}^\ominus = 247 \text{ kJ/mol}$)既可解决 CH_4 升值利用的问题,也可实现 CO_2 减排.当前,国内外的许多研究机构都致力于开发高活性和高稳定性的适合于工业应用的 CH_4 - CO_2 重整催化剂.原则上,周期表中第VIII过渡金属和Ru, Rh, Pd, Ir和Pt等贵金属都可以作为 CH_4 - CO_2 重整催化剂的活性组分.然而,事实上,只有Ni和上述贵金属具有实际意义.担载的贵金属是优良的重整催化剂,在高温下可使 CH_4 具有很高的转化率,却不会因为积炭而失活,但由于价格昂贵,其工业应用受到了限制. Ni基催化剂由于高活性和廉价易得^[1],被认为是 CH_4 - CO_2 重整最有前景的催化剂.

Ni-Mg-Al水滑石是阴阳离子插层组装的一系列超分子,经过焙烧制得的固体碱催化剂(LDO)具有介孔结构,用于催化 CH_4 - CO_2 重整反应表现出优异的催化性能. Xu等^[2]利用聚氧乙烯-聚氧丙烯-聚氧乙烯(P123)表面活性剂作为软模板剂蒸发诱导组装制备了具有介孔结构的Ni-Mg-Al(O)催化剂,该催化剂比表面积高、孔体积较大、孔径分布均匀,用于 CH_4 - CO_2 重整反应在 700°C , $\text{GHSV} = 15000 \text{ mL}/(\text{h} \cdot \text{g}_{\text{cat}})$ 和 $\text{CH}_4/\text{CO}_2 = 1/1$ 的条件下,反应100 h CH_4 的转化率仍保持在80%. Zhang等^[3]制备的Ni-Mg-Al水滑石催化剂在160 h反应时间内没有观察到失活. 本课题组^[4]前期以共沉淀法制备了Ni-Mg-Al-LDO催化剂,在 800°C 、 $\text{GHSV} = 8000 \text{ mL}/(\text{h} \cdot \text{g}_{\text{cat}})$ 和 $\text{CH}_4/\text{CO}_2 = 1/1$ 的条件下,2000 h反应后 CH_4 和 CO_2 的转化率仍保持在95%以上.

考虑到表面活性剂的引入可以调整水滑石的形貌、颗粒大小等性质^[5],可以解决共沉淀法因沉淀剂的加入使局部浓度过高产生团聚的弊端,可以显著改善催化剂中金属的分散度和结构性^[6]、控制不同晶面暴露及制备表面缺陷结构、实现对本征化学反应的调节^[7,8]和延缓积炭等^[9],在前期研究的基础上,本文采用表面活性剂辅助共沉淀法制备Ni-Mg-Al-LDO催化剂,考察了表面活性剂对Ni-Mg-Al水滑石前驱体的微观作用以及进一步对形成的复合氧化物的晶体结构、理化性质和Ni不同晶面暴露的影响,关联了催化剂结构和催化性能的关系.

2. 实验部分

2.1. 催化剂制备

Ni-Mg-Al固体碱催化剂采用表面活性剂辅助共沉淀法制备. 将一定量的 Na_2CO_3 溶于100 mL去离子水,表面活性剂溶于50 mL去离子水,依次加入四口烧瓶. 60°C 下同时将硝酸盐混合溶液((Ni+Mg)/Al的摩尔比为

3) 120 mL和NaOH溶液(1 mol/L)逐滴加入上述 $\text{Na}_2\text{CO}_3(n(\text{CO}_3^{2-})/n(\text{M}^{n+}) = 2/3)$ 和表面活性剂的混合溶液中,强力搅拌保持pH值为9.15. 滴加完成后,持续搅拌3 h,将所得悬浊液转入晶化釜中于 80°C 晶化24 h. 晶化完成后,对悬浊液进行抽滤,洗至 $\text{pH} = 7$. 滤饼在 80°C 下干燥过夜,再于 700°C (升温速率 $5^\circ\text{C}/\text{min}$)恒温焙烧6 h,焙烧之后的催化剂以-LDO命名, NiO的质量分数为10%. 未添加表面活性剂的催化剂命名为LDO,添加表面活性剂四丙基氢氧化铵(TPAOH)、P123、聚乙烯吡咯烷酮(PVP)和十六烷基三甲基溴化铵(CTAB)的催化剂依次命名为TH-LDO, P3-LDO, PP-LDO和CB-LDO.

2.2. 催化剂表征

催化剂前驱体的官能团鉴定采用Bruker Vertex70型红外光谱仪测定, KBr压片, 分辨率 4 cm^{-1} , 测量范围 $4000\text{--}400 \text{ cm}^{-1}$.

催化剂织构使用Micromeritics ASAP 2020型吸附仪测定, 采用BET和BJH公式计算催化剂的比表面积和平均孔径.

晶相结构在DX-2700型X射线衍射(XRD)仪上用连续扫描法测定($\text{Cu } K_\alpha$ 靶, $\lambda = 1.5405 \text{ \AA}$, 40 kV , 30 mA); 扫描范围 $2\theta = 5^\circ\text{--}85^\circ$, 扫描速率为 $8^\circ/\text{min}$, 步长 0.01° . 催化剂的晶粒大小采用Scherrer方程求得.

活性金属的分散状态和形貌采用FEITECNAI G²F-20型高分辨透射电子显微镜(HRTEM)测定.

催化剂活性位Ni的化合价状态和电子结合能采用Thermo Fisher公司Escalab 250型X光电子能谱(XPS)仪, 以单色化 $\text{Al } K_\alpha(h\nu = 1486.6 \text{ eV})$ 为X光源, 真空度优于 $2.0 \times 10^{-7} \text{ Pa}$. 样品测试时, 通过能为 30 eV , 步长 0.1 eV . 采用污染碳($\text{C } 1s \text{ } E_b = 284.6 \text{ eV}$)对样品进行荷电校正, 使用Sheirly法扣除背景.

催化剂的还原性质在TP-5000型(天津先权)程序升温吸附仪进行. 将50 mg焙烧后催化剂装入石英管微型反应器, 用纯He气在 150°C 下恒温吹扫30 min, 降温至 50°C 后切换5% H_2/N_2 的混合气($20 \text{ mL}/\text{min}$), 保持30 min后从 50°C 升至 900°C (升温速率 $10^\circ\text{C}/\text{min}$)进行程序升温还原(TPR), 热导检测器检测耗氢量.

积炭的氧化性质测定在TP-5000型程序升温吸附仪上进行. 将100 mg反应后催化剂装入石英管微型反应器, 用纯He气在 150°C 下恒温吹扫30 min, 降温至 50°C 后切换5% O_2/Ar 的混合气($20 \text{ mL}/\text{min}$)保持30 min, 然后从 50°C 升至 900°C 进行程序升温氧化(TPO)反应(升温速率 $10^\circ\text{C}/\text{min}$). 尾气使用HIDEN (QIC-20)型质谱检测,

绘制CO₂生成量与温度的关系曲线,以此来判断碳物种种类;以活性炭氧化作为标准计算积炭含量。

2.3. 催化剂评价

催化剂活性评价在常压固定床(内径8 mm)反应装置上进行,将焙烧后催化剂0.30 g与石英砂1.70 g (40–60目)混和均匀放入石英管反应器内。将石英管和热电偶置于反应器保温炉中,热电偶顶部感应部分插入反应炉至反应管外壁,紧贴催化剂床层。800 °C下用H₂/N₂ (V/V, 1/1)预还原2 h,而后切换原料气CH₄/CO₂ = 1/1, GHSV = 60000 mL/(h·g_{cat}),于不同温度下反应。反应尾气经冷凝除水后用上海海欣气相色谱仪(GC-950)检测(TDX-01型填充柱,热导检测器,Ar载气)。

3. 结果与讨论

3.1. 催化剂性能评价

课题组前期以无表面活性剂辅助共沉淀法制备的催化剂LDO,在800 °C, GHSV = 8000 mL/(h·g_{cat})和CH₄/CO₂ = 1/1的条件下已完成了2000 h的稳定性考察,CH₄和CO₂转化率始终保持在95%以上^[4]。本文为了缩短评价时间、提高催化剂筛选速度,采取了提高空速(GHSV = 60000 mL/(h·g_{cat}), CH₄/CO₂ = 1/1)以加速催化剂积炭失活的方法。图1为催化剂活性评价结果。可以看出,相对于未加表面活性剂的催化剂LDO,添加表面活性剂TPAOH有明显的促进作用,CH₄和CO₂初始转化率都在95%以上,而表面活性剂P123, PVP和CTAB表现出一定的抑制作用。值得注意的是,PP-LDO的CH₄初始转化率只有18%,而CB-LDO的CH₄初始转化率几乎为0,但随着反应的开始数小时内迅速达到顶点。可见,不同表面活性剂辅助合成的催化剂初活性差异很大,揭示了表面活性剂对新鲜催化剂结构和表面态的显著影响。

3.2. 催化剂活性分析

图2(a)是未焙烧样品的XRD谱。图中显示,所有样品均出现了水滑石化合物的特征衍射峰,对应于晶面(003), (006), (009), (015), (018), (110)和(113),没有发现任何相关的氧化物或氢氧化物的特征峰,表明制备的水滑石化合物较纯。图2(a)中,决定水滑石晶体中层间距的(003)晶面特征衍射峰强度高^[10]、对称性好、峰形尖锐,且(110)和(113)晶面衍射峰清晰可辨,表明合成的Ni-Mg-Al水滑石呈六方晶型结构并结晶良好。这也表明表面活性剂辅助共沉淀法可以制备结晶完美的Ni-Mg-Al-LDHs。表1是采用Scherrer方程计算的晶胞参数 a ($a = 2d_{(003)}$)和 c ($c = d_{(003)} + 2d_{(006)} + 3d_{(009)}$)的值,其中

a 代表层板上金属盐离子的平均半径;而 c 值与层板厚度、层板的电荷密度、层间阴离子的大小及层间水分子数量密切相关^[11]。由表1可知,加入表面活性剂TPAOH, PVP和CTAB都使晶胞参数 c 减小,表明层板正电荷密度增加,层板与层间阴离子间的库仑作用力增强;而加入P123晶胞参数 c 增大,表明层板正电荷密度减小,层板与层间阴离子间的库仑作用力减弱。TPAOH, PVP, CTAB的共同特点是都含有N原子,其中TPAOH和CTAB是季铵盐类化合物, PVP由于N与羰基相连,使其N也具有缺电子性,这是它们能增强层板与层间阴离子间的库仑作用力的原因。而P123为中性分子,没有缺电子中心且O原子上具有孤对电子,电子云密度较大,因此导致层板正电荷密度减小,层板与层间阴离子间的库仑作用力减弱。结合图1可知,总体上,能增强层板与层间阴离子间的库仑作用力的表面活性剂,亦即具正电性的表面活性剂对催化剂活性有利。

图2(b)是未焙烧样品水滑石前驱体的FT-IR谱,其中3543 cm⁻¹处的吸收归因于金属氢氧化物层间-OH的伸缩振动引起, 2925 cm⁻¹处的吸收归属为层间氢键与碳酸盐之间第二种-OH的伸缩振动, 1120 cm⁻¹红外吸收峰是C-N单键伸缩振动^[12], 1370和858 cm⁻¹可分别为CO₃²⁻伸缩振动和面外弯曲振动。1637 cm⁻¹的吸收是来自层间水分子(H-O-H和δH-O-H)的变形伸缩振动, 500–750 cm⁻¹是来自M-O-M键(M = Mg, Ni和Al)的伸缩振动^[13],属于水滑石骨架结构的特征峰,该峰的出现进一步证实了产物是规整的水滑石化合物。

图2(c)是Ni-Mg-Al-LDO催化剂经焙烧还原后样品的XRD图。图中 $2\theta = 36.4^\circ$, 43.4° , 62.9° 和 79.2° 为方镁石Mg(Ni,Al)O晶相的特征衍射峰^[14]。 $2\theta = 44.5^\circ$, 51.8° 和 76.3° 分别对应于Ni(111), (200), (220)晶面的特征衍射。由图2(c)可见Ni(111)和Ni(200)的结晶状态存在差异,最明显的是Ni(200)面从下到上逐次增加。为避免不同次测量带来的误差,以TH-LDO在 $2\theta = 44.5^\circ$ 处的肩峰为Ni(111)峰位置,以该位置的高度为Ni(111)强度计量,其与51.8°峰高比用以表示样品中Ni(200)的份额。计算得 $I_{\text{Ni}(200)}/I_{\text{Ni}(111)}$ 的顺序为: TH-LDO (27.7%) > LDO (25.4%) > P3-LDO (22.0%) > PP-LDO (14.3%) > CB-LDO (11.1%),该顺序与催化剂初活性顺序相吻合,暗示了Ni(200)对催化剂活性的意义。各催化剂Ni(200)面暴露程度不同的原因,可归结为不同的表面活性剂在前驱体形成时与不同晶面的作用能力不同,不同的表面活性剂会选择性地集中吸附在不同的晶面,从而降低了该表面

的自由能, 减缓该晶面的生长速度, 进而调控了金属粒子的尺寸和形貌^[15].

图3是催化剂焙烧还原后的HRTEM图. 图3(a–d), 分别对应于催化剂样品 TH-LDO, LDO, P3-LDO 和 PP-LDO, 由图可以观察到明显的 d 值为0.203和0.176 nm 的两个主要暴露晶面, 结合对应的傅里叶变换(FFT)图可以证实是Ni(111)和Ni(200)晶面, 与文献[16,17]的结果一致. 但在CB-LDO样品(图3(e))中没有发现Ni(200)面的存在. 这表明尽管前驱体在焙烧和还原处理后会发晶型变化及二次晶体生长, 但被表面活性剂保护的晶面的生长仍会受到抑制.

金属Ni的晶体结构为面心立方(fcc)结构, 按照fcc结构的对称性, 它们的侧面是交替的Ni(100)和Ni(111)晶面. Ni(200)是晶胞结构中Ni(100)晶面的二级衍射, (200)为干涉指数, (100)是晶面指数, 虽然两者代表的含义不同, 但在空间点群中的贡献相同, 所以XRD中Ni(200)可以等同于空间点阵的(100). 由于Ni(111)的平均 d 带中心能量较高, 不利于 CH_x 的解离, 而Ni(100)可以通过降低活化能垒促进 CH_x 物种的解离^[18]. 因此, 与Ni(111)相比, Ni(100)亦即Ni(200)面是 CH_x 解离的首选表面^[19], 这可以解释前述Ni(200)相对强度与活性的顺变关系.

图4是焙烧后样品的 H_2 -TPR谱, 图中370–866 °C的还原峰顶温度的差异表明Ni-Mg-Al-LDO中的NiO物种与介孔骨架之间形成了不同的相互作用. 根据文献, 370–450 °C 的还原峰归属于纯NiO的还原^[20,21]; 500–800 °C的还原峰对应于 Ni^{2+} 和 Al_2O_3 或 MgO 弱的相互作用^[22,23]; 大于800 °C的峰归属为Ni-Mg固溶体中 Ni^{2+} 的还原或Ni-Al尖晶石的还原^[24,25]. 其中高温还原峰温度顺序为: TH-LDO (866 °C) > LDO (840 °C) > P3-LDO (817 °C) > PP-LDO (787 °C) > CB-LDO (702 °C), 与初活性顺序一致, 说明与载体作用强的Ni金属粒子是提供催化活性位的主要位点. 文献报道^[26–28], 金属与载体的强相互作用(SMSI)可以使金属Ni颗粒与载体结合的更紧密, 分布更均匀, 不易还原, 同时可以抑制Ni颗粒的烧结和积炭, 进而对催化剂活性和稳定性有利.

图5是催化剂焙烧还原后的XPS谱, 分别有4个结合能位置. 结合能852.6 eV归属于 Ni^0 ^[29], 对应于 H_2 -TPR结果中 Ni^{2+} 和 Al_2O_3 或 MgO 弱的相互作用物种的还原; 结合能855.4和857.3 eV可分别归属于 Ni^{2+} 和 Ni^{3+} ; 861.2 eV是 $\text{Ni}^{2+} 2p_{3/2}$ 的卫星峰^[30,31]; 高结合能 Ni^{2+} 的出现可作为Ni-Al尖晶石存在的证据^[32]. 这表明焙烧还原后的催化剂样品表面存在 Ni^0 , Ni^{2+} 和 Ni^{3+} 多种Ni物种, 与TPR结果

一致, 即在800 °C的预还原温度下氧化态Ni难以被完全还原. 比较图4和图5可以发现, 归属于 Ni^0 和 Ni^{2+} , Ni^{3+} 的峰面积相对含量没有规律性的对应关系, 这可能是样品在做XPS测试前转移过程中存在不可避免地被氧化的结果. 然而不排除 Ni^{x+} ($x = 0, 2, 3$)间协同促进了反应的进行^[33].

图6是焙烧还原后催化剂的TEM图和Ni粒子尺寸分布统计. 粒子分布统计整体上小于XRD中的计算结果(见表2), 这是由于XRD测试时没有经过仪器宽化校正导致. 比较各催化剂Ni粒子的尺寸分布可以发现, TH-LDO, LDO和P3-LDO最可几粒径相差不大, 均在10 nm左右, 只是分布宽度略有不同; PP-LDO最可几Ni粒径约8 nm, 而CB-LDO的约6 nm, 前者分布宽度也是最窄的. PP-LDO催化剂Ni粒径小、分布窄可能源于PVP分子较强的与金属的配位能力以及对水滑石 c 值的压缩能力, 而CB-LDO相同的现象则完全源于对水滑石 c 值的压缩能力(c 值最小, 见表1). PP-LDO和CB-LDO的Ni粒径最小也得到TPR实验的支持(图4): 二者的主还原峰顶温度均不超过800 °C, 因此不能完全归属于Ni-Mg固溶体中 Ni^{2+} 的还原或Ni-Al尖晶石的还原^[24,25], 而应归属于高分散的、与 Al_2O_3 或 MgO 弱的相互作用^[22,23]的Ni氧化物粒子还原. 关联催化剂性能评价可以推断, 与 Al_2O_3 或 MgO 弱作用的Ni粒子对催化剂的初活性没有贡献.

选择具有代表性的TH-LDO, LDO和CB-LDO催化剂进行了织构性质的表征. 图7是焙烧后样品 N_2 -吸附-脱附等温线及其孔径分布图. 可以看出, TH-LDO, LDO和CB-LDO样品分别在相对压力 $p/p_0 = 0.5\text{--}0.6, 0.7\text{--}0.8$ 和 $0.8\text{--}0.9$ 时存在阶跃, 并伴有滞后环, 属于典型的IV型等温线, 表明其为典型的介孔材料. TH-LDO和LDO呈现H1型滞后环, 说明孔结构规整有序且孔径分布集中(见图7(b)). 而CB-LDO呈现H3滞后环, 说明孔的类型主要是由片状粒子堆积形成的狭缝孔, 而且对应的孔径较大, 孔径弥散(见表3和图7(b)), 表明CB-LDO固溶体中粒子在形成狭缝孔时会发生聚集^[34,35]. 表3为各催化剂样品的织构性质. 可见, 反应前各样品的织构参数差别很大, 但反应后大致趋于一致. 这与催化剂性能实验结果吻合, 即初活性差异大, 反应结束时活性趋同. 比较反应前各样品的比表面积和孔容: TH-LDO ($251 \text{ m}^2/\text{g}$) > LDO ($182 \text{ m}^2/\text{g}$) > CB-LDO ($106 \text{ m}^2/\text{g}$), 表明比表面积和孔容大的催化剂利于反应, 也说明表面活性剂对催化剂的初始织构有明显的调控作用.

3.3. 催化剂稳定性评价分析

图1给出了800 °C时各催化剂活性稳定性评价结果. 可见, 当CH₄转化率降至48%, TH-LDO, LDO和CB-LDO分别为35, 32和26 h. CB-LDO的明显特点是有一个活性诱导期, 在反应前4 h几乎没有活性, 之后至10 h活性迅速上升至最高值, 稳定4 h后开始失活. 图1还显示, 各催化剂样品开始失活时间不同, 但失活速率大致相同(基于图1 CH₄和CO₂转化率下降速度), 表明失活基本不受催化剂自身性质影响, 而主要由其它因素决定. 因此, 抑制失活应从探明失活的原因入手.

CB-LDO的活性诱导期可归结为部分细颗粒Ni物种被载体包裹的结果, 正如图6(e)所示, Ni颗粒图像模糊不清. Ni被包覆以致无法提供CH₄解离的活性位. 短的诱导期也表明随着持续的高温反应, 离子的热移动可迅速打破基体物的膜形态, 进行重构, 进而使Ni活性物种得以暴露, 使得催化反应得以进行(图8). 为证明这一推断, 本文又考察了反应温度对CB-LDO催化性能的影响.

图9(a–c)是CB-LDO在反应温度800, 900和1000 °C下的评价结果. 可以看出, 提高反应温度可以显著提高催化剂的活性和稳定性, 但未能导致诱导期消失, 只是一定程度上缩短了诱导期, 初步证实了CB-LDO中Ni的物种被载体包裹的推断. 对比焙烧还原后和不同温度反应后样品的XRD (图9(d))可以看出, 还原后的样品中没有检测到Ni和尖晶石的特征衍射峰. 800 °C反应后也观察不到尖晶石的特征衍射峰, 而900和1000 °C反应后样品出现了明显的Ni(111), Ni(200), Ni(220)和尖晶石(MgAl₂O₄, NiAl₂O₄)的特征衍射峰^[36,37], 可以推测, 在重整反应过程中生成(Ni, Mg)Al₂O₄尖晶石是导致Ni活性物种得以暴露的直接原因. 不同温度反应后样品的Ni(200)相对强度顺序(CB-LDO(35.6%)-1000 °C > CB-LDO (32.2%)-900 °C > CB-LDO (30.5%)-800 °C)进一步支持了前述催化活性与Ni(200)暴露程度相关的论断. 显然, 高温反应过程中不断形成NiAl₂O₄尖晶石对被载体包覆的Ni起到缓释作用, 逐渐暴露的Ni(200)晶面稳定了高温反应下的催化剂活性.

催化剂反应前的主要物相是NiO-MgO方镁石, 其晶体结构为立方体型, 而尖晶石为含八面体的结构, 由于立方八面体比立方体的表面积和表面自由能都低, 根据热力学原理, 立方八面体呈现更稳定的状态^[38]. Chen等^[39]报道尖晶石NiAl₂O₄可以明显抑制CH₄-CO₂重整中的积炭, 与本文中CB-LDO在1000 °C反应性能优于800和900 °C的结果一致. 显然, 对于某些特定的催化剂, 可以通过提高反应温度来提高活性和延长寿命. 理论上,

高温反应会加速活性金属烧结和积炭, 但同时也会引起催化剂物相重构, 从而导致有益的变化. 由表2中可清楚地看到, CB-LDO在900和1000 °C反应后的Ni粒子的平均尺寸明显小于800 °C下的Ni粒径. 因此, 高温反应必然会导致不利的变化不能一概而论.

为了验证上述结论的通用性, 我们将800 °C反应表现最优的TH-LDO催化剂在900 °C进行评价, 结果见图10. 可以看出, 在两个温度下反应的初活性相差无几, 然而, 反应中间段900 °C反应的活性较800 °C降低约10%, 之后, 失活速率较800 °C为慢, 这与CB-LDO不尽相同, 但高温下反应失活也较慢.

3.4. 催化剂失活分析

CH₄-CO₂重整过程中Ni基催化剂的失活主要是由于活性金属的烧结和表面积炭^[40–42]. 烧结会促使Ni颗粒的聚集, 进而使Ni颗粒长大. 本文中反应前(焙烧还原后)和反应后的Ni颗粒大小变化不明显, 说明烧结不是催化剂失活的主要原因, 失活是由积炭引起, 而不同表面活性剂催化剂失活速率相近也表明积炭一旦形成, 其生长速率将基本不受催化剂性质影响, 而是由积炭自身生长特性决定. 因此, 抑制积炭生成应从抑制积炭的初始产生入手.

CH₄-CO₂重整反应体系中, 反应式(1)和(2)是积炭的主要来源^[43–45]. 研究表明^[25,46,47], 反应后催化剂的TPO-MS耗氧峰顶温度分布在 < 250 °C为原子型碳(C_a), 300–500 °C为无定型碳(C_β), 600–700 °C石墨状碳(C_γ), 其中C_a和C_β具有活性, 大于300 °C就可以被氧化, 在反应体系中可以转化为合成气, 而C_γ难以转化为合成气, 在700 °C才能被氧化^[46,48,49]. 积炭的形貌反映了石墨化结晶的程度, 氧化温度会随着碳结晶度的增加而升高^[49,50].

图11(a)是在800 °C下反应后的各催化剂O₂-TPO-MS曲线. 在330–750 °C可以观察到明显的CO₂的信号. 由图11(a)和表2可见, TH-LDO, LDO和P3-LDO的表面积炭率较高, 特别是C_γ; 而PP-LDO和CB-LDO积炭速率较低. 这与TEM表征(图6)获得的最可几Ni粒度大小顺序基本一致, 映证了在较大颗粒金属Ni粒子表面容易产生积炭^[51,52]. 一般地讲, 小颗粒Ni⁰具有高的催化活性和抑制积炭性能, 大颗粒Ni⁰活性低并易于生成积炭. 本文中Ni粒径最小(以TEM统计结果为准)的催化剂PP-LDO和CB-LDO积炭率都很低, 而初活性也不高, 这

再次说明了除活性金属颗粒大小外,对活性起至关重要还有活性金属的晶面取向。

图11(b)是800 °C反应后催化剂的XRD图, $2\theta = 26^\circ$ 处出现了明显的石墨碳的特征衍射。图11(c–d)的TEM结果也表明活性金属被碳包覆。从图11(d)测得的包覆碳晶面间距为0.336 nm, 与文献[53]报道0.334 nm十分相近, 并且晶格线清晰, 表明积炭的石墨化程度很高, 与TPO-MS结果一致。

不同温度反应后CB-LDO样品的O₂-TPO-MS表征结果见图12(a)。由图可以看出, 反应温度越高, 石墨型积炭(C₇)越多, 但这不能说明是温度引起的, 因为三个样品的反应时间不同, 800, 900和1000 °C样品分别反应了34, 100和456 h, 如果计算平均积炭速率的话, 后者只有0.148 mg_c/(h·g_{cat}), 而800 °C样品高达1.679 mg_c/(h·g_{cat}) (见表2)。

图12(b)是CB-LDO催化剂1000 °C反应后粒子分布统计和TEM图, 其最可几粒径13 nm, 与表2结果(12.5 nm)接近, 但是与还原时的6 nm有长大的现象, 这是反应过程中催化剂物相反生重构的结果。TEM图中Ni周围可以清楚地观察到条纹间距为0.213 nm的包覆物, 与石墨碳层间距0.334 nm相差很大, 但与XRD中方镁石结构MgO(JCPDS 450946)的(200)晶面间距0.211 nm相近, 暗

示着CB-LDO中Ni被MgO包裹。这部分Ni在高温反应过程中由于相变化而得到了释放(图8), 暴露出了活性位Ni(200)面, 从而稳定了催化剂活性, 使CB-LDO在高温反应时表现出较优异的性能。

4. 结论

采用表面活性剂辅助共沉淀法可以实现对Ni-Mg-Al-LDHs前驱体层板厚度、层板电荷密度和层间距的有效调控, 进而影响新鲜Ni-Mg-Al-LDO催化剂的理化性质、微观结构以及晶体面取向; 表面活性剂通过自身的电荷特性和与金属离子的配位能力, 影响催化剂中金属粒子的大小以及促进或抑制Ni特定晶面的生长; 催化剂性能不仅取决于活性金属Ni粒度大小, 更取决于Ni(200)面暴露的相对比例; 高温下催化剂中物相的重构会使某些催化剂性能得到改善, 其原因归结为物相重构所带来的对Ni(200)晶面的缓释作用。结果表明, 积炭是导致Ni-Mg-Al-LDO催化剂的主要原因, 表面活性剂可在一定程度上影响积炭的初始生成, 但一旦形成积炭其生长速率将不主要受催化剂性质影响, 而是由积炭自身生长特性决定。因此, 抑制积炭生成应从抑制积炭的初始产生入手; 同时, 建立积炭-消炭的动态平衡、开发相应的催化剂才是根本。