

Carbon dioxide reforming of methane to synthesis gas over hexaaluminate $\text{ANiAl}_{11}\text{O}_{19-\delta}$ ($\text{A} = \text{Ca}, \text{Sr}, \text{Ba}$ and La) catalysts

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A series of A-modified hexaaluminates, $\text{ANiAl}_{11}\text{O}_{19-\delta}$ ($\text{A} = \text{Ca}, \text{Sr}, \text{Ba}$ and La) as new catalysts for carbon dioxide reforming of methane to synthesis gas, were prepared by decomposition of nitrates and calcination at high temperature. Nickel ions as active component were inlaid in the hexaaluminate lattices to substitute part of Al ions. The structure and properties of these samples were characterized using XRD, XPS, TPR and TGA techniques. The series of hexaaluminates exhibited significantly catalytic activity and stability at high temperature, for instance at 780 °C for 18 h, the conversion of CH_4 and CO_2 was kept over 91.0 and 93.7%, respectively, meanwhile no Ni sintering, phase transformation and catalyst deactivation due to carbon deposition were found. Besides, the modifier A in the mirror plane layer of the lattices showed different effects on reducibility and catalytic activity of transition metal Ni in the hexaaluminate lattices.

Keywords: hexaaluminate $\text{ANiAl}_{11}\text{O}_{19-\delta}$ catalysts, methane, CO_2 reforming, synthesis gas

1. Introduction

The process of carbon dioxide reforming of methane to synthesis gas has received considerable attention in recent years, because this process has several advantages over steam reforming or partial oxidation of methane. The synthesis gas produced possesses a low H_2/CO ratio and is more suitable for Fischer–Tropsch synthesis to liquid hydrocarbons and oxygenated derivatives. The process also has an important environmental implication, since both methane and carbon dioxide are greenhouse gases, which can be utilized to produce valuable feedstock for chemical industry [1–3].

Noble metals such as Ru, Rh, Pd, Pt and Ir, etc. have successfully been employed as highly active catalysts for CO_2 reforming of CH_4 to synthesis gas [3–5]. However, the high cost and limited availability of noble metals have stimulated researching for cheaper metals such as ferrous metals (Fe, Co and Ni) as worthwhile alternatives to noble metals [6]. Supported Ni-based material has been reported to be an effective catalyst for this reaction, but, it suffers a serious problem of deactivation due to carbon deposition, nickel sintering and phase transformation of the catalyst [3,7]. Therefore, it is very important to improve the state of supported Ni catalysts in order to overcome these disadvantages. Some researchers have greatly enhanced the catalytic activity and stability of Ni catalysts by using different supports, promoters and nickel precursor compounds [8–11]. In the present work, the authors describe a simple preparation method of Ni-based hexaalu-

minates $\text{ANiAl}_{11}\text{O}_{19-\delta}$ ($\text{A} = \text{Ca}, \text{Sr}, \text{Ba}$ and La), in which Ni ions as active component were inlaid in the hexaaluminate lattices to substitute part of Al ions. The reducibility and catalytic activity for the reaction of the catalysts were investigated. Iyi et al. studied the hexaaluminate crystal structure in detail [12]. Every hexaaluminate compound crystallizes in either the $\beta\text{-Al}_2\text{O}_3$ or the magnetoplumbite structure. Both of these structures consist of alternative stacking of a spinel block and a mirror plane; in addition, the structure type of hexaaluminates is determined by the charge and radius of the large modification cations in the mirror plane layer. Some hexaaluminates have been reported to be good catalysts for high-temperature catalytic combustion [13,14]. To date, few papers concerning Ni-substituted hexaaluminate used as catalyst for the topic reaction have been published [15,16].

2. Experimental

2.1. Catalyst preparation

All hexaaluminate catalysts, $\text{ANiAl}_{11}\text{O}_{19-\delta}$ used in this research ($\text{A} = \text{Ca}, \text{Sr}, \text{Ba}$ and La), were prepared as follows: alkaline earth metal or lanthanum nitrates, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ were dissolved in distilled water with a molar ratio of 1 : 1 : 11, respectively, then the aqueous solution was slowly added to a polyethylene glycol–isopropyl alcohol solution under magnetically stirring. The mixture was evaporated to dry at 80 °C, and stored in an oven to remove polyethylene glycol and to decompose the nitrates. After being ground into fine powder, the sample was cal-

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cined at 400 °C for 2 h, followed by calcination at 1250 °C for 5 h.

2.2. Characterization of the catalysts

The crystal structure of the calcined samples was determined by X-ray powder diffraction (XRD) (Shimadzu XD-3A diffractometer) using a Ni filter and Cu $K\alpha$ radiation, at 30 kV and 20 mA. Diffraction peaks recorded (for the 2θ value range) between 20° and 60° have been used to identify the structure obtained. The binding energy and chemical composition of surface elements of the catalysts were measured by X-ray photoelectron spectroscopy (XPS) (V.G. ESCA Mark II) using Al $K\alpha$ radiation. The measurements were operated at a pass energy of 50 eV and a step size of 0.05 eV. The amount of carbon deposited on the catalysts was determined by oxidation conducted using a thermogravimetric analyzer (TGA) (Perkin–Elmer TGA7).

The reducibility of hexaaluminates $\text{ANiAl}_{11}\text{O}_{19-\delta}$ was characterized by the temperature-programmed reduction technique (TPR). For this purpose 0.2 g of catalyst was embedded in a fixed-bed quartz tube with an inner diameter of 8 mm. Before the reaction, the samples were treated at 300 °C for 30 min and cooled to room temperature in Ar flow. Then, the reactor was heated from room temperature to 1200 °C at a linear heating rate of 20 °C/min in a 10% H_2/Ar mixture gas flow at a rate of 30 ml/min. The temperature was measured using a thermocouple located in the bed and the effluent gases were passed through a dryer filled with 5A molecular sieve. A gas chromatograph (Shimadzu GC-8A) equipped with a thermal conductivity detector (TCD) was employed.

2.3. Catalytic activity tests

The reforming reaction was carried out under atmospheric pressure in a tubular fixed-bed quartz reactor. A thermocouple was placed in the center of the catalyst bed to monitor the reaction temperature. The reactant mixture consisted of CH_4 and CO_2 with a molar ratio of 1:1 and flowed at a rate of 30 ml/min. 0.2 g of catalyst was embedded in the quartz tube with an inner diameter of 8 mm. Before reaction, the catalyst was reduced at 900 °C in a flow of 10% H_2/Ar mixture gas for 1 h. The exit gases (reactant/product mixtures) were analyzed by a gas chromatograph (Shimadzu GC-8A) equipped with a thermal conductivity detector (TCD) and Porapack-Q and 5A molecular sieve columns. The catalytic activities were investigated at temperatures ranging from 500 to 900 °C and the stability of the catalysts was conducted at 780 °C.

3. Results and discussion

3.1. Crystal structure and stability of hexaaluminates $\text{ANiAl}_{11}\text{O}_{19-\delta}$

Figure 1 shows the XRD patterns of hexaaluminates $\text{ANiAl}_{11}\text{O}_{19-\delta}$ ($A = \text{Ca}, \text{Sr}, \text{Ba}$ and La) before reaction. It

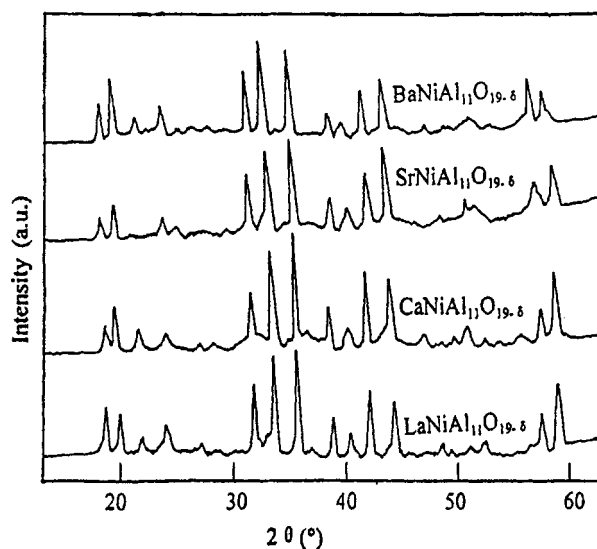


Figure 1. XRD patterns of hexaaluminates $\text{ANiAl}_{11}\text{O}_{19-\delta}$.

is found that the series of samples exhibit almost the same hexaaluminate crystalline structure, the diffraction peaks (2θ) being the same except for $\text{BaNiAl}_{11}\text{O}_{19-\delta}$: the characteristic diffraction peaks of $\text{ANiAl}_{11}\text{O}_{19-\delta}$ ($A = \text{Ca}, \text{Sr}, \text{La}$) are at 35.9°, 33.8° and 31.9°, respectively, and those of $\text{BaNiAl}_{11}\text{O}_{19-\delta}$ are at 35.6°, 33.1° and 31.7°, respectively. The reasons for the difference in 2θ are that the $\text{BaNiAl}_{11}\text{O}_{19-\delta}$ belongs to the $\beta\text{-Al}_2\text{O}_3$ -type structure and the others belong to the magnetoplumbite-type structure. The crystalline structure of the hexaaluminates obtained is consistent with that of the samples synthesized by the hydrolysis of metal alkoxides method and the aerogel-derived approach reported in [12,17–19]. Furthermore, it can also be observed that the crystal structure remained unchanged after the reforming reaction and TPR experiment, respectively, indicating that the $\text{ANiAl}_{11}\text{O}_{19-\delta}$ samples are extremely stable and only a part of Ni^{2+} ions in the hexaaluminate lattices can be reduced to Ni^0 at high temperature.

Table 1 gives the crystal phases observed by XRD analyses after calcination at various temperatures, implying that the key factors for precursors to transform into hexaaluminates are temperature and time of calcination. The formation of the phase with a hexaaluminate-type crystal structure begins at 1000–1100 °C and completes at 1250 °C for 5 h. When different alkaline earth metal nitrates are used as precursors of modifier A, some spinel-type oxides such as NiAl_2O_4 , SrAl_2O_4 and BaAl_2O_4 formed after calcination at 1100 °C.

Arai and coworkers suggested that in the case when a powder mixture of $\gamma\text{-Al}_2\text{O}_3$ and BaCO_3 is used, BaAl_2O_4 formed first which can easily sinter, and due to a slow diffusion-controlled solid state reaction with $\gamma\text{-Al}_2\text{O}_3$, does not allow the formation of the aimed phase. On the other hand, when an alkoxide method is used, BaAl_2O_4 does not form and the hexaaluminate phase is directly obtained from the amorphous precursors [20,21]. Noticeably in our case, a pure hexaaluminate can be obtained even if NiAl_2O_4 ,

Table 1
Crystallographic phases observed by XRD.

| Catalyst | Crystallographic phases | |
|--|---|--|
| | 1100 °C | 1250 °C |
| CaNiAl ₁₁ O _{19-δ} | α-Al ₂ O ₃ , NiAl ₂ O ₄ , CaNiAl ₁₁ O _{19-δ} | CaNiAl ₁₁ O _{19-δ} |
| SrNiAl ₁₁ O _{19-δ} | α-Al ₂ O ₃ , SrAl ₂ O ₄ , NiAl ₂ O ₄ , SrNiAl ₁₁ O _{19-δ} | SrNiAl ₁₁ O _{19-δ} |
| BaNiAl ₁₁ O _{19-δ} | α-Al ₂ O ₃ , BaAl ₂ O ₄ , BaNiAl ₁₁ O _{19-δ} | BaNiAl ₁₁ O _{19-δ} |
| LaNiAl ₁₁ O _{19-δ} | LaNiAl ₁₁ O _{19-δ} | LaNiAl ₁₁ O _{19-δ} |

Table 2
Binding energy of surface elements of hexaaluminates ANiAl₁₁O_{19-δ} (eV).

| A | ANiAl ₁₁ O _{19-δ} | A 2p _{3/2} (3d _{5/2}) | Ni 2p _{3/2} | Al 2p | O 1s |
|----|--|--|----------------------|-------|-------|
| Ca | CaNiAl ₁₁ O _{19-δ} | 347.3 | 856.4 | 74.1 | 531.2 |
| Sr | SrNiAl ₁₁ O _{19-δ} | 133.9 | 856.4 | 74.1 | 531.2 |
| Ba | BaNiAl ₁₁ O _{19-δ} | 780.4 | 856.4 | 74.1 | 531.2 |
| La | LaNiAl ₁₁ O _{19-δ} | 835.6 | 856.2 | 74.1 | 531.0 |

Table 3
Chemical composition of surface elements of hexaaluminates ANiAl₁₁O_{19-δ}.

| A | ANiAl ₁₁ O _{19-δ} | A (%) | Ni (%) | Al (%) | O (%) |
|----|--|-------|--------|--------|-------|
| Ca | CaNiAl ₁₁ O _{19-δ} | 0.59 | 0.60 | 41.98 | 56.82 |
| Sr | SrNiAl ₁₁ O _{19-δ} | 0.57 | 0.69 | 42.15 | 56.59 |
| Ba | BaNiAl ₁₁ O _{19-δ} | 0.57 | 0.74 | 42.14 | 56.54 |
| La | LaNiAl ₁₁ O _{19-δ} | 0.60 | 0.77 | 41.76 | 56.86 |

SrAl₂O₄ and BaAl₂O₄ formed as intermediates, the formation of crystalline phase NiAl₂O₄, SrAl₂O₄ and BaAl₂O₄ does not prevent formation of the aimed hexaaluminate oxides. However, when lanthanum nitrate as a precursor of A is superior to alkaline earth metal nitrates, the Ni-based lanthanum hexaaluminate LaNiAl₁₁O_{19-δ} formed easily and no spinel-type compounds appear after treating the precursors at rising temperature of calcination.

3.2. Oxidation state and chemical composition of surface elements

Table 2 gives the binding energy of surface elements of hexaaluminates ANiAl₁₁O_{19-δ}. It can be seen that the binding energy of surface elements Ni, Al and O is not affected by A, that is, their valence state in the surface does not change in the A-modified samples. Thus, it can be concluded that their oxidation states are Ni²⁺, Al³⁺ and O²⁻, respectively. Based upon the binding energy data, it can also be assured that the oxidation states of modifier A in the samples are Ca²⁺, Sr²⁺, Ba²⁺ and La³⁺, respectively.

Table 3 shows the chemical composition of surface elements of the hexaaluminate catalysts ANiAl₁₁O_{19-δ}. It is found that the Ni content is extremely lower in the surface than in the bulk. It can be suggested that in our case surface segregation of one of the components takes place. It is believed that this is the main reason for effective catalytic activity over the reduced hexaaluminates ANiAl₁₁O_{19-δ} for this reaction at high temperature. In the meantime, mod-

ification by A in the mirror plane has different effects on Ni content in the surface phase. Among the ANiAl₁₁O_{19-δ} samples, Ni content increases with an increase in ionic radius for alkaline earth metal modification, however, modification by La makes LaNiAl₁₁O_{19-δ} have the highest Ni content in the surface phase.

3.3. Reducibility of hexaaluminate ANiAl₁₁O_{19-δ} catalysts

As shown in figure 2, the TPR profiles of ANiAl₁₁O_{19-δ} indicate that A-modified Ni-based hexaaluminates ANiAl₁₁O_{19-δ} exhibit almost the same reduction profiles in the shape and need extremely higher reduction temperature than nickel oxides, starting to be reduced at about 870 °C, meaning that hexaaluminates ANiAl₁₁O_{19-δ} have reduction stability at high temperature. At the same time, every sample of this series of ANiAl₁₁O_{19-δ} gives only one reduction peak which does not drop down even up to 1100 °C. The XRD patterns of the sample after TPR measurement demonstrated that the reduced hexaaluminates still possessed the same crystalline structure as that obtained before reduction. This illustrates that the Ni ions inlaid in the hexaaluminate lattices are extremely stable, have only oxidation state Ni²⁺ and only a part of Ni²⁺ can be reduced to Ni⁰ at 1100 °C. Besides, we also observed that the reducibilities of ANiAl₁₁O_{19-δ} compounds are different due to the difference of modifiers. When the alkaline earth metals are employed, the first reduction temperature decreases with an increase in the ionic radius of A. However, La-modified hexaaluminate LaNiAl₁₁O_{19-δ} gives the lowest first reduction temperature. The above mentioned fact illustrates that the reducibility of hexaaluminates ANiAl₁₁O_{19-δ} depends strongly on the properties of transition metal Ni, and is also affected by kind, ionic radius and valence of modifiers.

3.4. Catalytic activity

We examined the catalytic activity of the reaction over the reduced hexaaluminate ANiAl₁₁O_{19-δ} catalysts under atmospheric pressure. The catalytic activities of the reduced ANiAl₁₁O_{19-δ} for the reaction in a temperature range between 500 and 900 °C are shown in figure 3, indicating that the conversions of both CH₄ and CO₂ rapidly increased with increase in the reaction temperature, and 100% of their conversion was reached at 890 °C, meaning that hexaaluminates ANiAl₁₁O_{19-δ} are significantly active for this reaction.

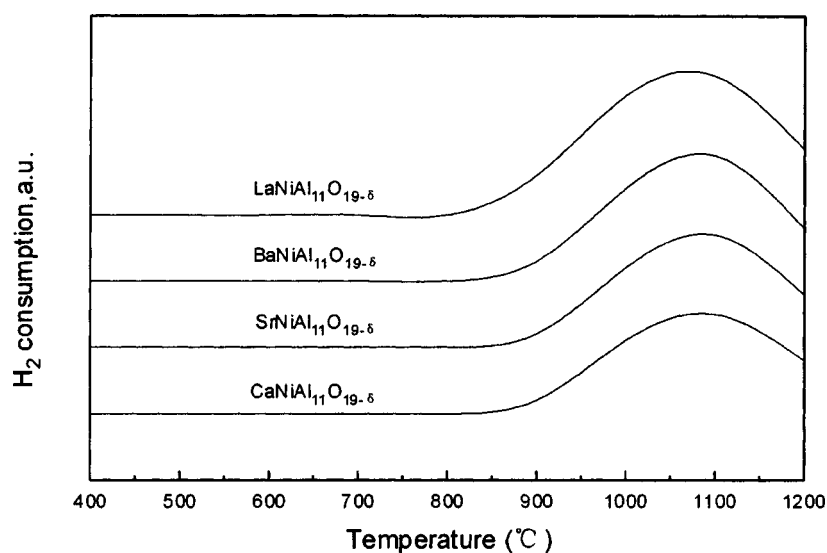
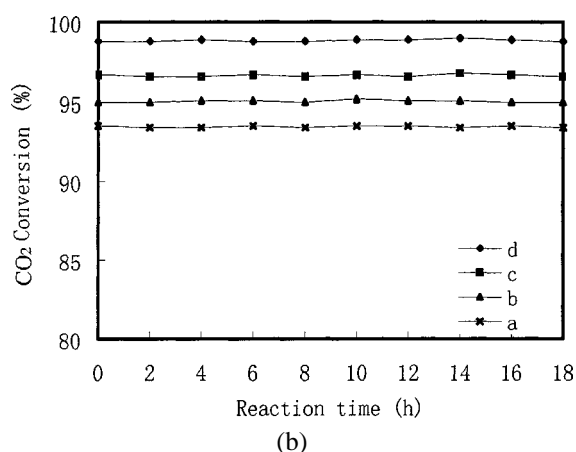
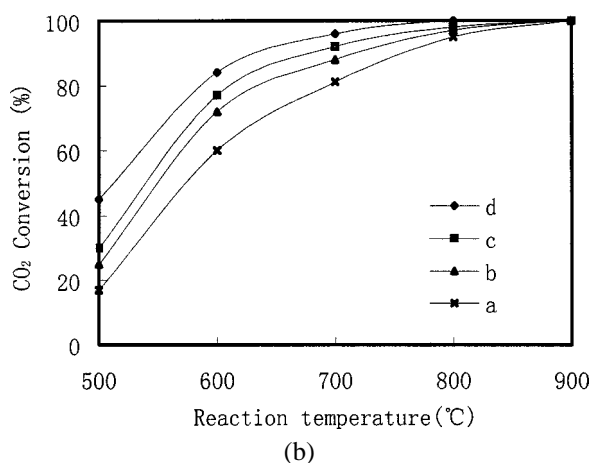
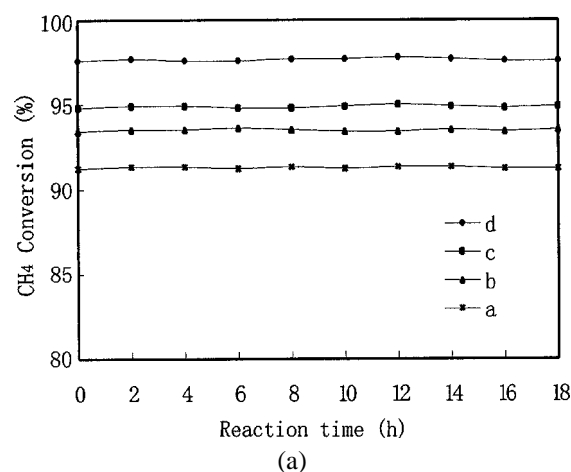
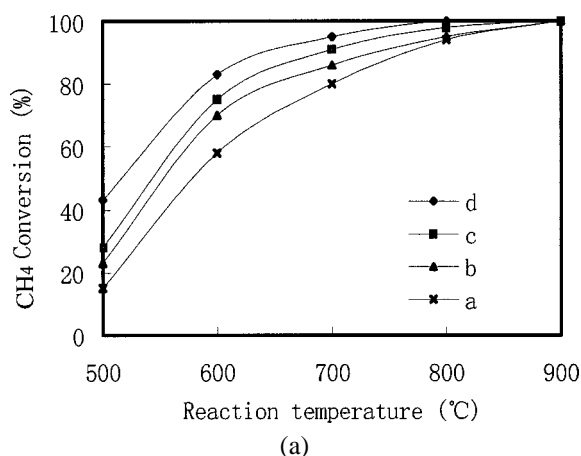
Figure 2. TPR profiles of hexaaluminates $\text{ANiAl}_{11}\text{O}_{19-\delta}$.

Figure 3. Temperature dependence of the conversions of CH_4 and CO_2 over the reduced hexaaluminates $\text{ANiAl}_{11}\text{O}_{19-\delta}$: (a) $\text{CaNiAl}_{11}\text{O}_{19-\delta}$, (b) $\text{SrNiAl}_{11}\text{O}_{19-\delta}$, (c) $\text{BaNiAl}_{11}\text{O}_{19-\delta}$ and (d) $\text{LaNiAl}_{11}\text{O}_{19-\delta}$. $V(\text{CH}_4):V(\text{CO}_2) = 1:1$, flow rate 30 ml/min, catalyst 0.2 g.

Figure 4. The stability of the reduced hexaaluminates $\text{ANiAl}_{11}\text{O}_{19-\delta}$ at 780 °C: (a) $\text{CaNiAl}_{11}\text{O}_{19-\delta}$, (b) $\text{SrNiAl}_{11}\text{O}_{19-\delta}$, (c) $\text{BaNiAl}_{11}\text{O}_{19-\delta}$ and (d) $\text{LaNiAl}_{11}\text{O}_{19-\delta}$. $V(\text{CH}_4):V(\text{CO}_2) = 1:1$, flow rate 30 ml/min, catalyst 0.2 g.

The stability of the reduced hexaaluminates $\text{ANiAl}_{11}\text{O}_{19-\delta}$ was examined at 780 °C. As shown in figure 4, these catalysts exhibited effective catalytic activity

and stability, and provided over 91.0 and 93.7% conversion of CH_4 and CO_2 , respectively, which remained unchanged for 18 h of time on stream. The amount of carbon de-

posited on the reduced hexaaluminates ANiAl₁₁O_{19-δ} was extremely low, reached 1.618, 1.699, 1.980 and 1.554 wt% (also for 18 h), respectively, and no Ni sintering and phase transformation were found, suggesting a main reason for the significantly catalytic activities and stability of ANiAl₁₁O_{19-δ} catalysts. In the meantime, it can be observed that modifiers have different effects on the catalytic activity of the reduced hexaaluminates ANiAl₁₁O_{19-δ}, that is, the catalytic activity increases with an increase in the ionic radius of the modifiers. However, LaNiAl₁₁O_{19-δ} shows the best catalytic activity and the lowest amount of carbon deposition. The conversions of CH₄ and CO₂ over it remained higher than 97.4 and 98.6%, respectively. The catalytic activities of alkaline-earth-metals-modified samples are lower than that of the La-modified one. The activity sequence of the reduced hexaaluminates is LaNiAl₁₁O_{19-δ} > BaNiAl₁₁O_{19-δ} > SrNiAl₁₁O_{19-δ} > CaNiAl₁₁O_{19-δ}, illuminating that the stability and catalytic activity of ANiAl₁₁O_{19-δ} are mainly determined by Ni in the hexaaluminate lattices, and also sensitively affected by modifier A.

4. Conclusion

A series of hexaaluminate ANiAl₁₁O_{19-δ} catalysts have been prepared, in which the transition metal Ni as active component is inlaid in the hexaaluminate lattices. All ANiAl₁₁O_{19-δ} catalysts show effective catalytic activities and stability for CO₂ reforming of methane at high temperature. The catalytic properties and reducibility of the catalysts are strongly dependent on the radius and valence of the modifier ions. It is worthy to point out that this series of catalysts are resistant to nickel sintering, phase transformation and carbon deposition.

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