

Production of the hydrogen by methane steam reforming over nickel catalysts prepared from hydrotalcite precursors

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Abstract

Catalysts were prepared from hydrotalcite precursors, characterized and tested in the reaction of methane steam reforming to produce hydrogen. The precursors were synthesized by: the traditional technique, with co-precipitation of Ni, Mg and Al nitrates with carbonate; co-precipitation of Mg and Al nitrates with pre-synthesized nickel chelate and anion-exchange of NO_3^- of hydrotalcite with nickel chelate. The oxides were analyzed using atomic absorption spectrophotometry, specific surface area, X-ray diffraction (XRD), temperature programmed reduction (TPR) with H_2 , catalytic tests and elemental analysis. The catalytic tests demonstrated high methane conversion, high activity for hydrogen production and high stability during the time of reaction for a molar ratio in the feed $\text{H}_2\text{O}:\text{CH}_4 = 2:1$.

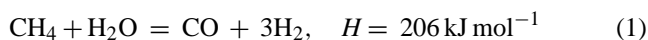
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1. Introduction

Steam reforming of hydrocarbons, especially of methane, which is the principal constituent of natural gas, is the most widely used and generally the most economical way to produce hydrogen. Supported nickel catalysts are used industrially, although research shows that these catalysts, at low steam:methane ratios in the feed, suffer from coke formation, leading to catalyst deactivation. Coke is formed at high temperatures between the domain of the metallic nickel and the metal-support interface, liberating small particles of nickel from the support and covering the surface with large amounts of fibrous carbon, thus destroying the catalyst structure and killing its activity [1].

Methane steam reforming can be represented by the reactions (1) and (2).



Supported metal catalysts are normally prepared by wet impregnation of various supports. This method may produce some heterogeneity in the distribution of metal on the surface, leading to a lowest dispersion of metallic species favoring coke formation. The use of precursors containing the metal homogeneously distributed through the catalytic structure may, after the calcinations and reductions, result in the formation of highly-dispersed and stable metal particles on the surface. Some studies show that the use of hydrotalcite precursors minimizes coke formation since all the cations are homogeneously distributed inside the brucite-type sheets of the hydrotalcite anionic clay structure [2].

Hydrotalcites, a family of anionic clays, are known as layered double hydroxides (LDHs). They may be represented by the general formula:



and consist of layers of brucite M(II)(OH)_2 , which as a result of partial substitution of divalent by trivalent cations, acquire excess positive charge. This excess charge is compensated by the incorporation of anions into the interlayer

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space. An important feature of these compounds is the relative facility of anion exchange [3]. There is practically no restriction the nature of the anions, except that they should not form strong complexes with the cation present. It is known that the interlayer space can be used to introduce metals in the anionic form (chromates, chelates and others) [4]. Tsyganok et al. [5], recently reported a novel method of hydrotalcite synthesis, where they suggested the introduction of nickel into the structure Mg–Al (LDH), using the fact that Ni(II) has the ability to react with the anionic chelating agent of EDTA⁴⁻, making the highly stable species [Ni(EDTA)]²⁻ [5].

In light of the above points, the goal of this work is the preparation and characterization of catalysts from hydrotalcite precursors obtained by the traditional technique and by chelates. These catalysts will be tested in the reaction of methane steam reforming at different temperatures and molar ratios of fed steam to carbon in the feed.

2. Experimental

2.1. Synthesis

The hydrotalcite precursor containing nickel was prepared by three different methods: traditional, co-precipitation and anion-exchange. Precipitation was performed at a temperature of 63 °C pH 10, controlled by addition of 1 M aqueous NaOH solution.

2.1.1. Traditional technique (*tr-NiMgAl-CO₃*)

Ni-containing Mg–Al layered double hydroxide was prepared by dropwise addition of an aqueous solution (100 mL) containing Ni(II), Mg(II) and Al(III) nitrates (5, 25 and 10 mmol) to a continually stirred solution of sodium carbonate (30 mmol in 200 mL). The resulting suspension was kept under agitation at 63 °C for an hour. Next, the precipitate was aged at the same temperature for 18 h without stirring. The precipitate, having a pale green color was separated by filtration, rinsed with deionized water (until complete removal of Na⁺ cations), dried in air at 80 °C for 24 h and reserved [5].

2.1.2. Chelation-based techniques

For the following syntheses a nickel complex chelate was utilized. This was prepared by adding nickel nitrate solution (50 mmol in 100 mL of water) to tetrasodium EDTA solution (50 mmol in 100 mL of water) at 63 °C. This chelated solution was denominated (NIY)²⁻ [5].

- Co-precipitation method (cp-MgAl–NiY): this method consists in dropwise addition of an aqueous solution (100 mL) of Mg(II) and Al(III) nitrates (30 and 10 mmol) to stirred (NIY)²⁻ solution, at pH 10. The resulting suspension was stirred at 63 °C for 1 h and

received the same treatment as in the traditional technique.

- Anion-exchange method (ae-MgAl–NIY): in this method, the hydrotalcite Mg–Al (LDH) was first obtained by addition of Mg(II) and Al(III) nitrates (30 and 10 mmol dissolved in 100 mL of water) to 1 M NaOH solution, with stirring. The suspension was stirred for 1 h and then aged as in the other techniques. (NIY)²⁻ solution was added to this suspension, stirred at room temperature. The suspension was then stirred for 24 h at room temperature and the precipitate received the same treatment as above.

The mixed oxides were obtained by calcination at 500 °C in air for 15 h and denominated tr-oxide, cp-oxide and ae-oxide according to the hydrotalcite precursor.

2.2. Characterization techniques

The chemical composition of Ni–Mg–Al oxides was determined in a Hitachi Z-8100 atomic absorption spectrophotometer with lamp current 12.5 mA, wavelength 240.7 nm and a flame of Ar/C₂H₂ (2.2 L min⁻¹).

Specific surface area of mixture oxides was measured by adsorption of N₂ according to BET method using a NOVA Data Analysis.

X-ray diffraction (XRD) patterns were collected at room temperature in a URD-6 Carl Zeiss diffractometer with Cu K α radiation ($\lambda = 1.54056 \text{ \AA}$). The spectra were scanned in the range $2\theta = 3\text{--}80^\circ$ at a rate of 2° min^{-1} .

Temperature-programmed reduction (TPR) with hydrogen (H₂-TPR) of the catalysts was performed in Micromeritics Chemisorb 2705 equipment, using 50 mg of catalyst and a temperature ramp from 25 to 1000 °C at $10^\circ \text{ C min}^{-1}$. A flow rate of the 30 mL min⁻¹ of 5% H₂/N₂ was used.

Coke formation on the catalyst during tests of activity was measured by element analysis in an Elemental Analyzer CE1110, model CHNS-0, using 3 mg of the sample in a tin capsule, with the furnace at 1200 °C.

2.3. Catalytic tests

Catalytic activity was tested in a fixed-bed tubular quartz micro-reactor, so as to analyze the activity for hydrogen production, product distribution and coke formation as a function of the time of reaction. Before the reaction, the catalysts were reduced in a flow of hydrogen (50 mL min^{-1}) at 550 °C for 1 h, after which were heated to the reaction temperature under flowing nitrogen.

During the catalytic tests, both the reaction temperature and the steam:carbon molar ratio in the feed was varied. The effect of reaction temperature variation was analyzed for a constant feed molar ratio of H₂O_v:CH₄ = 4:1, the reaction being performed at 650 and 750 °C with a CH₄ flow of 40 mL min^{-1} . The effect of varying the feed molar ratio was analyzed at 750 °C, with a CH₄ flow of 40 mL min^{-1} , and the ratios used were H₂O_v:CH₄ = 4:1 and

Table 1
Composition of mixed oxides and specific surface area

Synthetic-LDH	Composition of oxides	Specific surface area ($\text{m}^2 \text{g}^{-1}$)
tr-NiMgAl-CO ₃	NiMg ₁₇ Al ₂ O ₂₁	129.0
cp-MgAl-NiY	NiMg _{17.4} Al _{1.6} O _{20.8}	167.1
ae-MgAl-NiY	NiMg _{17.2} Al _{1.8} O _{20.9}	200.6

2:1. The ratio $\text{H}_2\text{O}_v:\text{CH}_4 = 2:1$ is stoichiometric. Finally, to study deactivation process by coke, the drastic feed molar ratio $\text{H}_2\text{O}_v:\text{CH}_4 = 0.5:1$ was used.

Reaction products were analyzed by gas chromatography (GC) using a GC-3800 Varian chromatograph equipped with two detectors and Porapak N (He carrier gas) and molecular sieve 13X packed columns (N₂ carrier gas).

3. Results and discussion

3.1. Chemical composition and specific surface area of the mixed oxides

The chemical compositions and specific surface areas of the three mixed oxides are shown in Table 1. Whereas the compositions were similar for all methods of synthesis employed, the specific surface area of the catalysts prepared by anion-exchange with Ni chelate was higher than that achieved by the traditional method. The co-precipitation method gave intermediate values.

3.2. X-Ray diffraction (XRD)

Fig. 1 presents the XRD patterns of the synthesized hydroxalate precursors and the mixed oxides obtained from them by thermal decomposition. The patterns show that all precursors produced peaks characteristic of hydroxalate structure, the traditional method leading to the highest crystallinity. The thermal treatment resulted in changes of the phase structure and chemical composition. Calcination at 500 °C for 15 h resulted in the disappearance of the layered structure of hydroxalate and formation of peaks attributed to NiO and MgO

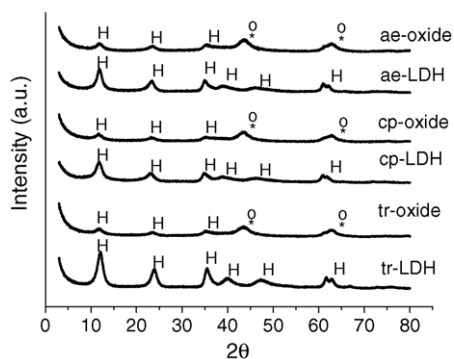


Fig. 1. Powder XRD patterns for synthesized LDH precursors and respective oxides. H: hydroxalate; (*) MgO; (°) NiO.

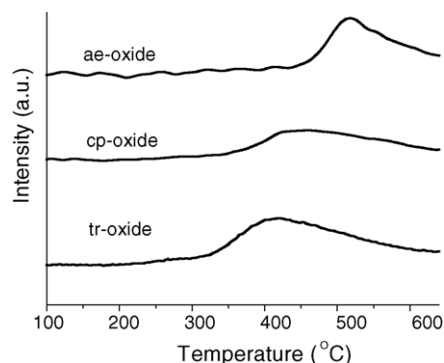


Fig. 2. Patterns of TPR of tr-oxide, cp-oxide and ae-oxide.

phases. No formation of solid solution was observed, since the temperature of calcination was not enough for this phase to occur [6].

3.3. Temperature-programmed reduction (TPR)

The TPR patterns of mixed oxides are presented in Fig. 2, where one reduction peak can be seen, starting above 300 °C, that can be attributed to the reduction of Ni²⁺ in the NiO phase. The position of this peak was different for each method of preparation and the anion-exchange method showed the highest stability of the NiO phase. Chmirlarz et al. [6] demonstrated another peak at about 950 °C, related to reduction of the spine phase NiAl₂O₄. This peak is not shown here because in this work the catalyst was activated at 550 °C.

3.4. Catalytic tests

The CH₄ conversions of all the catalyst, with a feed of molar ratio $\text{H}_2\text{O}_v:\text{CH}_4 = 4:1$ at 650 and 750 °C, are shown in Fig. 3.

All catalysts showed good activity in the 8 h of reaction. At 750 °C, the catalysts prepared with chelated Ni gave the best conversions of methane. At 650 °C, the methane conversion obtained with ae-NiMg_{17.2}Al_{1.8}O_{20.9}, was significantly lower than at 750 °C, whereas for cp-NiMg_{17.4}Al_{1.6}O_{20.8}, the change in the temperature did not influence the methane conversion.

Fig. 4 shows plots of hydrogen yield with a molar ratio $\text{H}_2\text{O}_v:\text{CH}_4 = 4:1$ in the feed at temperatures 650 and 750 °C. In Table 2 it is seen that the coke formation was low for all

Table 2
Amount of coke, after 8 h of reaction, with molar ratio $\text{H}_2\text{O}_v:\text{CH}_4 = 4:1$ at 650 and 750 °C

Catalyst	Temperature reaction (°C)	Amount of coke (%)
tr-NiMg ₁₇ Al ₂ O ₂₁	650	2.40
tr-NiMg ₁₇ Al ₂ O ₂₁	750	2.24
cp-NiMg _{17.4} Al _{1.6} O _{20.8}	650	1.78
cp-NiMg _{17.4} Al _{1.6} O _{20.8}	750	2.31
ae-NiMg _{17.2} Al _{1.8} O _{20.9}	650	0.89
ae-NiMg _{17.2} Al _{1.8} O _{20.9}	750	1.09

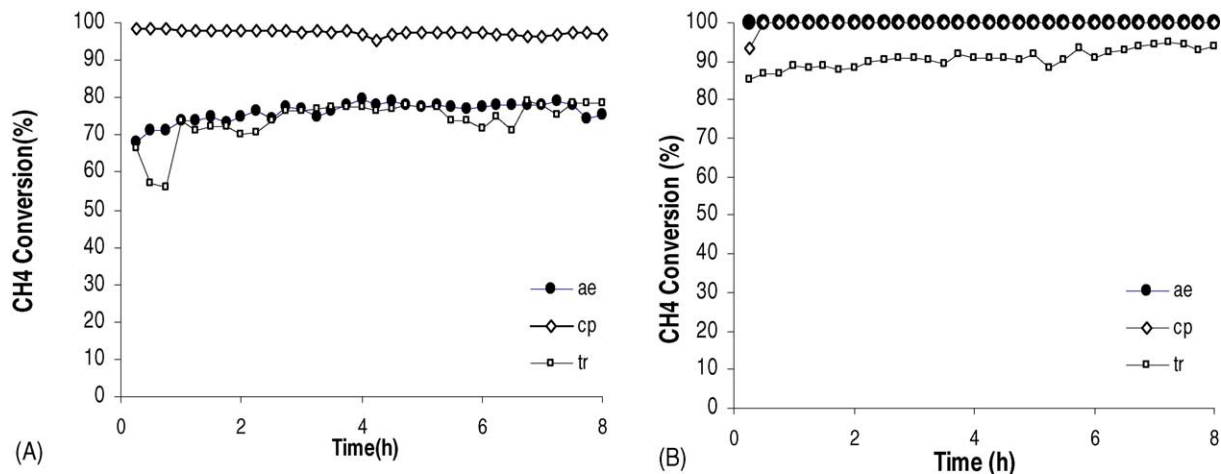


Fig. 3. Methane conversion for molar ratio of feed $H_2O_v:CH_4 = 4:1$, at reaction temperature: (A) $650\text{ }^\circ\text{C}$ and (B) $750\text{ }^\circ\text{C}$.

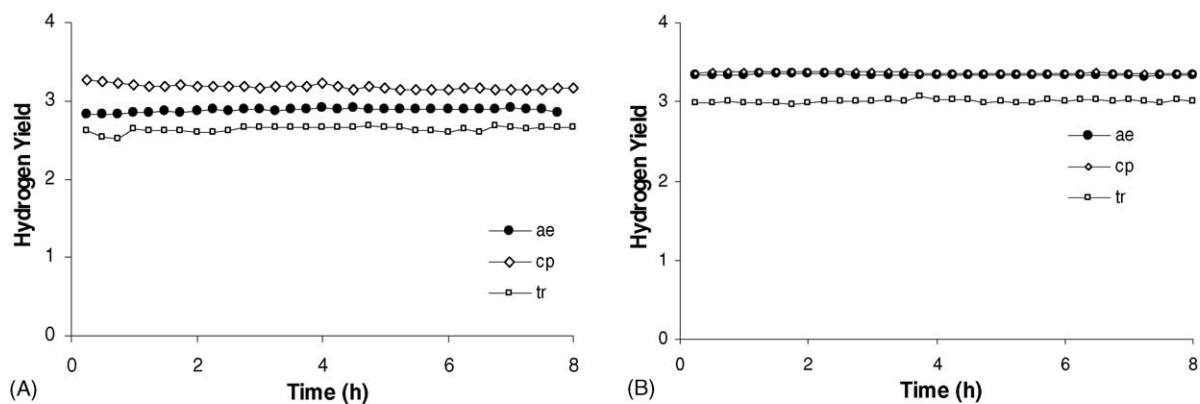


Fig. 4. Hydrogen yield with molar feedratio $H_2O_v:CH_4 = 4:1$ at temperature (A) $650\text{ }^\circ\text{C}$ and (B) $750\text{ }^\circ\text{C}$, for catalysts: tr-NiMg₁₇Al₂O₂₁; cp-NiMg_{17.4}Al_{1.6}O_{20.8}; ae-NiMg_{17.2}Al_{1.8}O_{20.9}.

Table 3
Product yield in methane steam reforming for several feed molar ratio at $750\text{ }^\circ\text{C}$

Catalyst	Molar ratio $H_2O_v:CH_4$	H_2 Yield (average)	CO Yield (average)	CO_2 Yield (average)	H_2/CO (average)
Tr-NiMg ₁₇ Al ₂ O ₂₁	4 ($650\text{ }^\circ\text{C}$)	2.63	0.43	0.42	6.12
	4	3.00	0.73	0.33	4.11
	2	2.40	0.76	0.11	3.15
	0.5	0.99	0.24	0.02	4.12
Cp-NiMg _{17.4} Al _{1.6} O _{20.8}	4 ($650\text{ }^\circ\text{C}$)	3.17	0.44	0.52	7.20
	4	3.37	0.58	0.46	5.81
	2	2.37	0.64	0.12	3.70
	0.5	1.06	0.30	0.01	3.53
Ae-NiMg _{17.2} Al _{1.8} O _{20.9}	4 ($650\text{ }^\circ\text{C}$)	2.88	0.32	0.56	9.00
	4	3.34	0.66	0.41	5.1
	2	2.44	0.70	0.10	3.48
	0.5	1.00	0.28	0.02	3.57

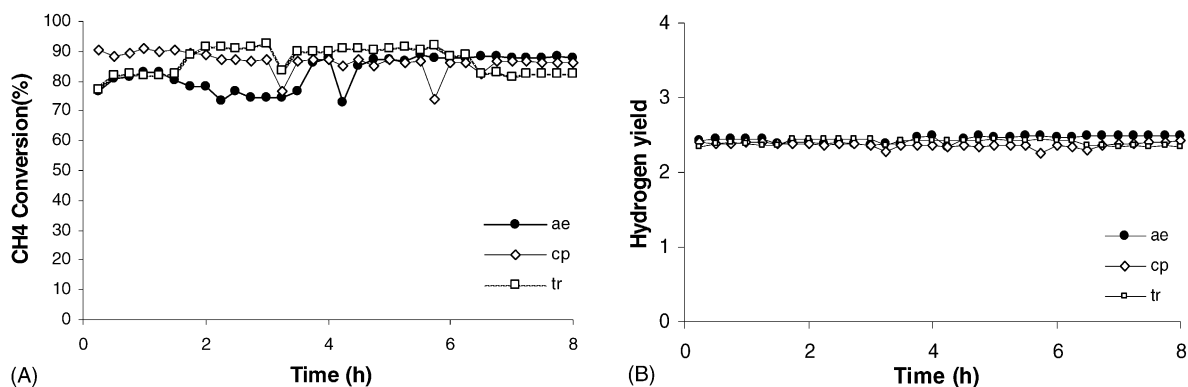


Fig. 5. (A) Methane conversion with a feed of molar ratio $H_2O_v:CH_4 = 2:1$ at $750^\circ C$. (B) Hydrogen yield: tr-NiMg₁₇Al₂O₂₁; cp-NiMg_{17.4}Al_{1.6}O_{20.8}; ae-NiMg_{17.2}Al_{1.8}O_{20.9}.

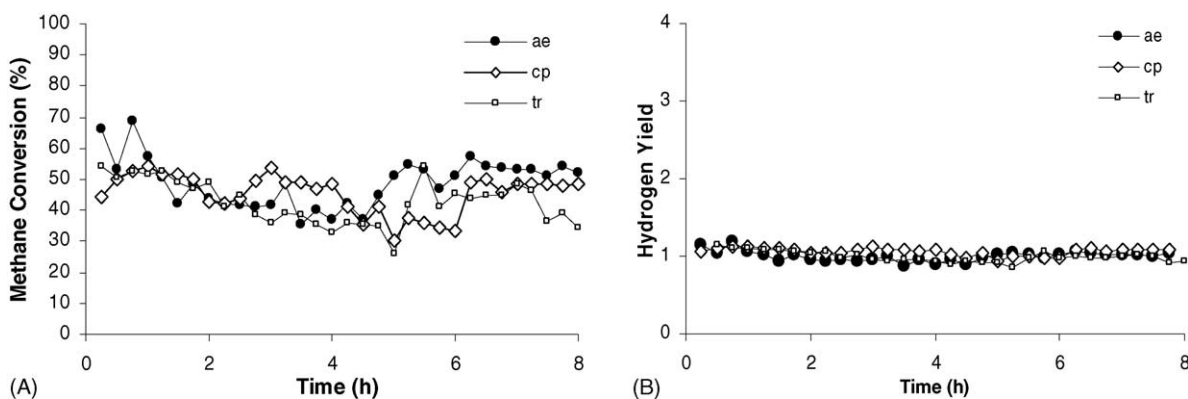


Fig. 6. (A) Methane conversion with a feed molar ratio $H_2O_v:CH_4 = 0.5:1$ at $750^\circ C$. (B) Product yield: tr-NiMg₁₇Al₂O₂₁; cp-NiMg_{17.4}Al_{1.6}O_{20.8}; ae-NiMg_{17.2}Al_{1.8}O_{20.9}.

catalysts, confirming the idea that hydrotalcite provides the most homogeneous catalysts.

As expected the decrease in temperature from 750 to $650^\circ C$ decreased the yield of CO in relation to CO₂ (according Table 3), because the formation of CO (reaction (1)) is an endothermic process and thus inhibited by the fall in temperature, which favored CO₂ formation (reaction (2)) as it is exothermic process.

Fig. 5(A) shows the methane conversion over 8 h, with feed molar ratio $H_2O_v:CH_4 = 2:1$ at $750^\circ C$. All catalysts showed activity and stability, throughout the 8 h of reaction, at this low steam to carbon ratio. The decrease in proportion of steam in the feed led to a decrease in the conversion of methane. The hydrogen yield for each catalyst is plotted in Fig. 5(B). With all cata-

lysts, the CO₂ yield was little, because the low molar ratio of steam to methane is unfavorable to its formation. These catalysts did not favor coke formation, according to Table 4.

Fig. 6(A) displays the methane conversion with a feed of molar ratio $H_2O_v:CH_4 = 0.5:1$. These tests were done to analyze the stability of catalysts in drastic feed conditions. Note that the catalysts were not deactivated in the 8 h of tests, showing their high stability for this reaction.

4. Conclusions

It has been demonstrated that catalysts obtained via hydrotalcite are active and stable for methane steam reforming. The low quantity of carbon formed on the catalysts surface confirmed the hypothesis that the structure of hydrotalcite layers leads to a homogeneous distribution of the active phase. Comparing the different methods of preparation, it was shown that the precursors obtained by means of Ni chelates were the most active in converting methane, with a high hydrogen

Table 4

Amount of coke after 8 h reaction with molar ratio $H_2O_v:CH_4 = 2:1$ at $750^\circ C$

Catalyst	Amount of coke (%)
tr-NiMg ₁₇ Al ₂ O ₂₁	2.77
cp-NiMg _{17.4} Al _{1.6} O _{20.8}	0.97
ae-NiMg _{17.2} Al _{1.8} O _{20.9}	2.99

yield, probably because they provided the best distribution of the active phase.

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