



CO₂ reforming of CH₄ over Co–Mg–Al mixed oxides prepared via hydrotalcite like precursors

Cédric Gennequin*, Maryam Safariamin, Stéphane Siffert, Antoine Aboukais, Edmond Abi-Aad

Université Lille Nord de France, F-59000 Lille, France Unité de chimie environnementale et interactions sur le vivant EA 4492, Université du Littoral Côte d'Opale, 145 avenue Maurice Schumann, 59140 Dunkerque, France

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ABSTRACT

Co_xMg_{6-x}Al₂ (with $x = 0, 2, 4,$ and 6) mixed oxides catalysts were synthesized via hydrotalcite precursors. The catalytic performance and stability were studied in dry reforming of methane. Regardless of the amount of coke deposited on the Co₆Al₂HT500 catalyst, no loss of activity was observed during 24 h on stream indicating that part of this carbon is not poisonous. Co₄Mg₂Al₂HT500 was undergoing a severe deactivation after 11 h on stream. The XRD result revealed an important sintering phenomenon of metal particles. Co₂Mg₄Al₂HT500 has shown a stable performance for 24 h on stream without any deactivation or coke deposition, displaying very good stability. This performance was explained by the stability of crystallite size of metal particles and by the presence of MgAl₂O₄ phase known for its basic properties.

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1. Introduction

CO₂ reforming of methane (CH₄ + CO₂ → 2CO + 2H₂ ($\Delta H_{298}^\circ = 247$ kJ/mol)) presents a double interest due to the production of syngas and the fact of consuming carbon dioxide; this latter is an important agent of the greenhouse effect. Dry reforming of methane is generally performed with catalysts based on noble metals [1] or transition metals as nickel or cobalt [2–4]. The major problem of this reaction is the deactivation by carbon deposition [5]. To minimize this problem, several authors suggest the use of supports possessing basic characters, and/or allowing to better dispersion of the active phase [6,7]. The objective of this work is the catalytic study of mixed oxides issued of Co/Mg/Al hydrotalcites (LDH) with different molar ratio as precursors for the dry reforming of methane. Cobalt is known as an active metal for this reaction [3] and mixed oxides obtained from hydrotalcites-like compounds exhibit basic properties as well as higher dispersion of the active phase [8]. Moreover catalyst surface basicity helps to suppress carbon deposition by promoting the activation of CO₂ on the surface of catalysts. Indeed, an interesting way to obtain mixed oxides catalysts is through the use of hydrotalcites as precursors.

2. Experimental

Four samples with different Co and Mg contents were synthesized using hydrotalcite method [9]: Co_xMg_{6-x}Al₂HT with $x = 0, 2, 4,$ and 6 . The calcination treatment of solids was performed under a flow of air (4 Lh⁻¹/2 °C min⁻¹ 4 h at 500 °C). Differential thermal and thermogravimetric analyses (DTA/TG) (Netzsch STA 409 equipped with a microbalance) were conducted in air at a heating rate of 5 °C min⁻¹ (25–1000 °C). The structure of solids was analyzed at room temperature by X-ray diffraction (XRD) technique using a Bruker D8 Advance diffractometer equipped with a copper anode ($\lambda = 1.5406$ Å). Diffraction patterns were recorded over a 2θ range of 4–80° and using a step size of 0.02 and a step time of 6 s. The mean crystallite sizes were estimated using the Scherrer equation. Catalytic tests were performed under atmospheric pressure. 100 mg of powder samples are placed in fixed bed quartz reactor. The reactants and products are analyzed with an on-line in a Varian 3600 chromatograph equipped with a CTRI column and a thermal conductivity detector. Before testing, calcined catalysts were treated with pure nitrogen (25–400 °C; 10 °C min⁻¹), after the sample is reduced or not with pure hydrogen flow (25–800 °C; 10 °C min⁻¹). Then the reactor is fed with the reagent gas mixture diluted with Ar (CH₄/CO₂ = 1), with a total flow rate of 100 mL min⁻¹.

The determination of methane and carbon dioxide conversions were calculated as follows:

$$X_{\text{CH}_4 \text{ conversion}} (\%) = \frac{(\text{CH}_4)_{\text{in}} - (\text{CH}_4)_{\text{out}}}{(\text{CH}_4)_{\text{in}}} \times 100$$

* Corresponding author at: Unité de chimie environnementale et interactions sur le vivant EA 4492, Université du Littoral Côte d'Opale, 145 avenue Maurice Schumann, 59140 Dunkerque, France. Tel.: +33 3 28 65 82 61.

E-mail address: cedric.gennequin@univ-littoral.fr (C. Gennequin).

Table 1
XCH₄/XCO₂, CO₂/CO, H₂/CH₄ ratio versus temperature and theoretical equilibrium CH₄ and CO₂ conversions.

T (°C)	XCH ₄ /XCO ₂	CO ₂ /CO	H ₂ /CH ₄
Co₆Al₂HT500			
450	0.94	0.58	1.13
550	1.43	0.62	1.40
650	1.11	0.53	1.57
750	1.01	0.51	1.62
Co₄Mg₂Al₂HT500			
450	0.16	0.86	1.86
550	0.86	0.54	1.48
650	1.05	0.51	1.54
750	1.08	0.48	1.49
Co₂Mg₄Al₂HT500			
450	0.63	0.62	1.31
550	0.84	0.55	1.46
650	0.94	0.53	1.55
750	0.99	0.50	1.61
Thermodynamic equilibrium (at 700 °C)		XCO ₂ or XCH ₄	72.3%

$$\text{XCO}_2 \text{ conversion (\%)} = \frac{(\text{CO}_2)_{\text{in}} - (\text{CO}_2)_{\text{out}}}{(\text{CO}_2)_{\text{in}}} \times 100$$

The different ratio is presented in Table 1 and carbon balances were calculated as follows:

$$\text{H}_2/\text{CO ratio (for example)} = \frac{\text{moles of H}_2 \text{ produced}}{\text{moles of CO produced}}$$

$$\text{Carbon balance} = \frac{(\text{CH}_4)_{\text{out}} + (\text{CO}_2)_{\text{out}} + (\text{CO})_{\text{out}}}{(\text{CH}_4)_{\text{in}} + (\text{CO}_2)_{\text{in}}} \times 100$$

The product selectivity is represented as the molar ratio of H₂/CO. The comparisons of the activities of these catalysts were primarily characterized by the conversion and the product selectivity criteria.

3. Results and discussion

3.1. Catalysts characterization

A detailed characterization of these catalysts can be found elsewhere [9]. In summary, the calcination at 500 °C of “HT” samples leads to a mixture of three oxide spinel phases: Co₃O₄, CoAl₂O₄ and Co₂AlO₄. Fig. 1a presents the XRD patterns of the reduced samples before test. For all samples Co⁰ is observed. For Co₂Mg₄Al₂HT500 and Co₄Mg₂Al₂HT500, the presence of spinel phase such as MgAl₂O₄ and CoAl₂O₄ is observed. For Co₆Al₂HT500, the peaks corresponding to the CoAl₂O₄ spinel structure are observed. The partial Co⁰ oxidation into CoAl₂O₄ spinel takes place

during the XRD analysis. This result indicates the stability of this structure under air at ambient temperature.

3.2. Catalytic activity

Solids did not show significant activity without reduction pretreatment (Fig. 2a). The low reforming activity can be assigned to the absence of metallic phase which is necessary to the adsorption and the activation of the reactants [4]. In the case of Co_xMg_{6-x}Al₂HT catalysts, reduction pre-treatment at 800 °C (1 h under pure H₂ flow 40 mL min⁻¹) strongly influenced the activity and selectivity. Fig. 2a–d illustrates the evolution of methane and CO₂ conversions obtained, at various temperatures, for reduced catalysts. The initial activity by comparison of methane conversion (Fig. 2a) follows the order: Co₆Al₂HT500 > Co₄Mg₂Al₂HT500 > Co₂Mg₄Al₂HT500 > Mg₆Al₂HT500.

The calculation of the equilibrium conversion for CO₂ reforming of methane at 700 °C for a CH₄/CO₂ feed ratio of 1/1 at atmospheric pressure is added in Table 1. This calculation is based on the assumption that only reforming reaction occurs without any side reactions. As the equivalent reaction stoichiometric, the CH₄ and CO₂ conversions should be equal and the H₂/CO ratio should be unity at all temperatures. However, the results obtained on CO₂ reforming of methane have discrepancies with the equilibrium results. The CO₂ conversion is different from that of CH₄ and the H₂/CO ratio is below unity (Table 1 and Figs. 2 and 3c). These results reveal that unfavourable reactions have strong influence on the performance of the reforming reaction and contribute to the reactants consumption without being strictly accounted for in equilibrium calculation as shown the studies of Haag et al. [10] and Avila-Neto et al. [11]. Their data show that the experimental result appears above the equilibrium curves, suggesting the formation of coke on the surface of the catalysts [11].

As illustrated in Fig. 3a, an amount of water is formed at the temperature range from 450 to 700 °C and reached a maximum at 550–600 °C beyond which the water yield decreased and the water formation is suppressed at higher temperatures. In parallel, at the same temperature range, an amount of carbon is formed as shown in Fig. 3b by an important negative carbon estimation. This result can be attributed to two reactions: the reverse water–gas shift reaction (CO₂ + H₂ → CO + H₂O (ΔH₂₉₈° = 41 kJ/mol)) which led to the formation of CO and water and the reverse carbon gasification reaction (CO + H₂ → C + H₂O (ΔH₂₉₈° = -131 kJ/mol)) which led to the formation of carbon and water (Fig. 3a and b). During the reverse water–gas shift reaction, CO₂ react with H₂ to produce CO and water in accordance with the experimental ratio presented in Table 1 (the ratio are lower than those provided by the dry reforming reaction only, for example H₂ is consumed and CO is produced which leads to

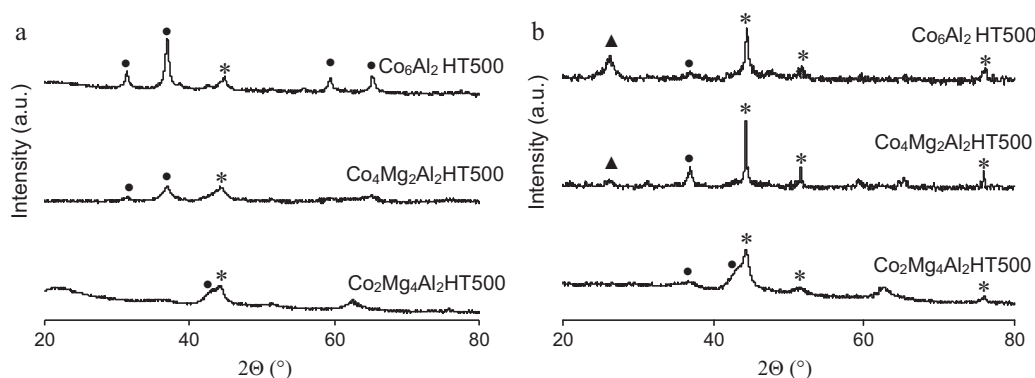


Fig. 1. XRD patterns of Co_xMg_yAl₂HT500 after H₂ reduction (a) and after catalytic test (b). *: Co⁰; JCPDS 150806; ●: spinel (CoAl₂O₄; JCPDS: 822239; MgAl₂O₄; JCPDS: 211152) ▲: graphite carbon; JCPDS 751621.

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