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Carbon dioxide reforming of methane on modified $Ni/\alpha\text{-}Al_2O_3$ catalysts

D. Halliche, R. Bouarab, O. Cherifi, M.M. Bettahar *

Laboratoire de Chimie du Gaz Naturel, Institut de Chimie, USTHB, PO Box 32, El Alia, 16111 Bab-Ezzouar, Algeria

Abstract

We have studied the CO_2-reforming of methane at atmospheric pressure in the range temperature 550–730°C on $Ni/\alpha\text{-}Al_2O_3$ catalysts modified by Fe, Co, Cu and Ce, respectively. The obtained results show that the activities depend on the CO_2/CH_4 ratio, the nature of the metal additives and the reaction temperature. The order of activity is Ni, Ni–Co, Ni–Ce > Ni–Cu ≫ Ni–Fe. The effect of the additives is attributed to their interaction with the nickel supported active phase. When CH_4 is replaced by H_2 in the presented reaction, no effect of the metal additives on the activities is observed and the CO_2 conversions are sensibly lower. These results let us think that the contribution of the reverse gas shift reaction is less important than expected in the overall process of the methane CO_2-reforming.

Keywords: Methane, CO_2 reforming of; Nickel catalysts

1. Introduction

Carbon dioxide reforming of methane is attracting much interest in academia and industry since it produces syngas [1–8]:

$$CH_4 + CO_2 \rightarrow 2CO + 2H_2 \qquad (1)$$

a highly versatile feedstock (synthesis of clean fuels or oxygenates, for example) from the cheapest carbon containing materials. The reaction is particularly interesting when natural gas is composed of methane and carbon dioxide.

Nickel supported catalysts [1–4] and noble metals [4] are found to be the most active catalysts and one of the most important problems in carrying out this reaction is coke deposition which deactivates the catalyst [4–6]. Nickel based catalysts are more prone to cocking than noble metals based catalysts are [4]. Copper additive increases coking of Ni/SiO_2 catalysts without dramatic effect on their activity whereas stability to coking decreases sharply for nickel supported on Al_2O_3, MgO, ZrO_2 [7]. On the other hand, carbon-free CO_2-reforming can be achieved on Ni/SiO_2 [5] or Ni/MgO–CaO [3] or in the presence of sulfur-poisoned $Ni/\alpha\text{-}Al_2O_3$ catalyst [4]. Thus, for the nickel-based catalysts, the activity and the stability to coke deposition seems to depend strongly on the nature of the support [2,3,5,7] and on the presence of additives [4,7].

These results prompted us to undertake a systematic study of the effect of metal additives (Fe, Co, Cu, Ce) on the performances of Ni/α-

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* Corresponding author. Correspondence to: M.M. Bettahar, Lab. de Catalyse et Spectrochimie, URA 0414, ISMRA, 6, blvd. du Marechal Juin, F-14050 Caen Cedex, France. Fax. (+33) 31452822.

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Al_2O_3 catalyst for the CO_2/CH_4 reaction. The CO_2/H_2 reaction has also been studied in parallel since it is believed to be a constituent reaction in the many steps involved in the CO_2-reforming of methane.

2. Experimental

2.1. Catalysts preparation

The α-alumina support was obtained by calcination of γ-alumina (Merck) 6 h at 1200°C under flowing air ($1.2\ l\ h^{-1}$, $5°C\ min^{-1}$ heating rate). Metal nitrates (Merck) were used as precursors in the preparation of the catalysts. The reference Ni/α-Al_2O_3 catalyst was prepared by conventional impregnation, followed by drying overnight at 110°C and calcination 6 h at 700°C under flowing air ($1.2\ l\ h^{-1}$, $5°C\ min^{-1}$ heating rate. The Ni-M/α-Al_2O_3 (M = Fe, Co, Cu, Ce) catalysts were prepared by impregnation of the calcined reference catalyst with the appropriate metal nitrate and following the same procedure as described above.

2.2. Characterization

The catalysts were characterized by the BET method on a Coultronics 2100D apparatus. The XRD spectra were recorded on a Philips PW1710 diffractometer.

2.3. Catalytic testing

The catalytic performances were carried out in a fixed-bed quartz tubular reactor with 0.1 g samples at atmospheric pressure at a total flow rate of $1.3\ l\ h^{-1}$. The reactant gas feed (Air Liquide) consisted of mixtures of CO_2/CH_4 (4/1) for the CO_2-reforming of methane and CO_2/H_2 (3/1) for the reverse shift reaction. All the catalysts were reduced overnight in a flow of H_2 at 600°C in-situ before testing and the catalytic performances were determined by raising the operating temperature from 550°C (660°C) to 730°C (700°C). The reactants and products were analyzed on line using TCD gas chromatograph equipped with a carbosieve column. Each reaction temperature was maintained constant until the corresponding steady-state was reached (no sensible deactivation is observed with time on stream in the operating conditions).

3. Results and discussion

3.1. Characterization

The surface area of Ni/α-alumina ($5.5\ m^2\ g^{-1}$) is sensibly higher than that of the support ($3.7\ m^2\ g^{-1}$) due probably to corrosion occurring during the calcination steps. On the other hand, the addition of Fe, Co, Cu and Ce to the reference catalyst decreases strongly ($0.7–1.3\ m^2\ g^{-1}$) its surface area, this drop arising either from an effect of the second calcination step at 700°C for the modified catalyst or/and from strong interactions between the present phases.

The spectra of the XRD study show sharp bands corresponding to well crystallized solids. The expected NiO and α-Al_2O_3 phases are present in all the catalysts. Two oxidized phases appear for the cobalt, copper and cerium additives ($CoO–Co_2O_3$, $CuO–Cu_2O$ and $CeO–CeO_2$, respectively) whereas the iron additive is detected as Fe_2O_3 phase.

3.2. Catalytic performances in the CO_2/CH_4 reaction

The products formed were CO, H_2 and H_2O and the carbon balance shows that coke deposited also.

The effect of the ratio CO_2/CH_4 (1.3–4.9) on the activity of the unmodified Ni catalyst is shown in Fig. 1. It appears that the conversions reach a maximum as the ratio increases. This maximum (63.1% for methane conversion and 41.4% for carbon dioxide conversion) is obtained with a ratio $CO_2/CH_4 = 4.0$. The same trends are observed for coke deposition as ex-

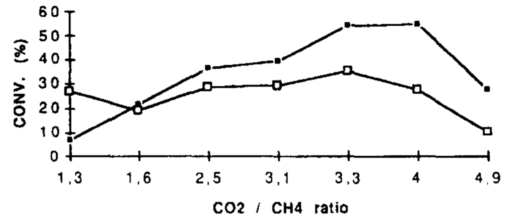

Fig. 1. Effect of the CO_2/CH_4 ratio on the activity of Ni/α-Al_2O_3 catalyst at 600°C. Symbols: ■ CH_4; □ CO_2.

pressed by the carbon balance values. On the other hand, the values of the H_2/CO (1.2–1.5) ratio are higher than unity, implying that other reactions than reaction (1) occur, notably the CH_4 coking reaction. It is worthwhile to note that a maximum of the rate of the CO_2/CH_4 ratio has also been reported recently [8].

The influence of the additives on the catalytic performances depends on their nature and the observed order of methane or carbon dioxide conversions are: Ni, Ni–Co, Ni–Ce > Ni–Cu ≫ Ni–Fe. The same trends are observed for the carbon monoxide yield, notably at low reaction temperature (Fig. 2).

These trends are not related to the surface areas. Indeed, for example, Co or Ce promotes activities similar to that of the reference catalyst whereas their surfaces areas (ca. 1.0 m^2 g^{-1}) are far more smaller than that of this catalysts (5.5 m^2 g^{-1}). The explanation may lie in a possible interaction between nickel and the metal additive as have shown the XRD study for Co, Cu and Ce additives in the calcined catalysts. For the Fe additive, this interaction may be related to amorphous phases not detected by XRD or may occur during the reduction step or under the reaction conditions.

These results are in good agreement with those reported in literature for SiO_2 supported catalysts [1,5,7] and notably those showing that Ni–Cu/SiO_2 catalyst is less active than Ni/SiO_2 catalyst [7]. Experiments on the behaviour of Co, Ce, Cu and Fe as active supported phases in the methane CO_2-reforming reaction are in hand in view of a better understanding of their effect as additive phases of the Ni/α-Al_2O_3 catalyst.

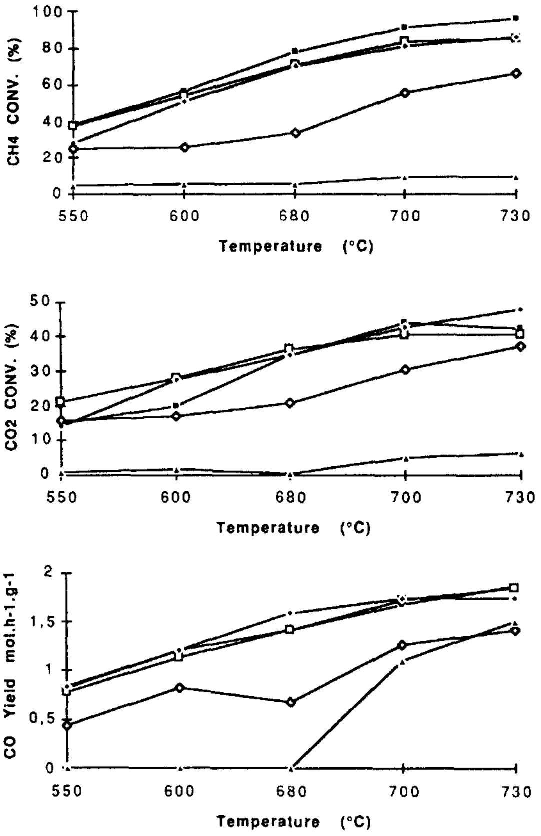

Fig. 2. Catalytic performances for the CO_2/CH_4 reaction as a function of temperature. Symbols: □ Ni–Co, ■ Ni, ▲ Ni–Fe, ◆ Ni–Ce, ◇ Ni–Cu.

As the observed relative activities (Fig. 2) may also be related to the kinetics of coking [1,4–6], it is of interest to examine the relative activities for coke deposition. The carbon balance values (Fig. 3) show that coke deposition depends also on the nature of the additive and on the reaction temperature. Thus, the relative

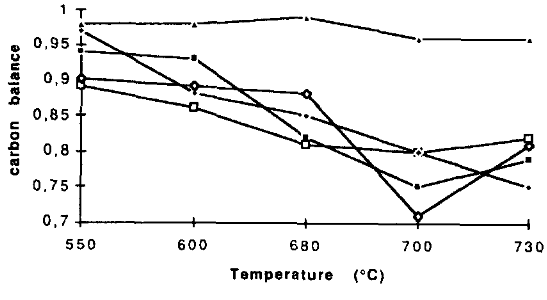

Fig. 3. Carbon balance for the CO_2/CH_4 reaction as a function of the temperature. (symbols same as in Fig. 2).

Table 1
Performances of the modified Ni/α-Al_2O_3 catalysts in the CO_2/H_2 reaction at 650°C

Catalyst	Ni	Ni–Co	Ni–Ce	Ni–Cu	Ni–Fe
CO_2 conversion (%)	22.0	23.1	16.4	16.0	16.7
CO yield (%)	12.0	14.0	14.4	14.0	12.7
C balance	0.90	0.91	0.98	0.98	0.96

order of carbon deposition at 700°C for example is: Cu > Ni > Co, Ce ≫ Fe. These results confirm that copper favours coking as reported on SiO_2 supported nickel catalysts [7]. However, they are less expected concerning iron additive since no coke seems to be formed, in contrast with what happens with Fe/SiO_2 catalyst [5]: in this case the very fast loss of activity is accompanied by high carbon deposition [5]. So, we think that the effect of the iron additive on catalytic performances of the α-alumina supported nickel phase is rather related to some specific interaction, the nature of which remains to be determined.

3.3. *Catalytic performances in the CO_2/H_2 reaction*

To study the CO_2/H_2 reaction in parallel to the CO_2/CH_4 reaction. We replaced in the CH_4 by H_2 with a ratio of $CO_2/H_2 = 3$ which is comparable both to the ratio of the feed gases and to the mean ratio observed in the exit gases in the above study.

The obtained results show that the features of the CO_2/H_2 reaction, are somewhat different from that of the CO_2/CH_4 reaction (results obtained at 650°C are reported in Table 1): (i) No great influence of the additives is observed on the nickel phase activity: whatever the reaction temperature, the total conversion (13%–28.9%) and the CO yield (11.8%–14.4%) are quite identical for all catalysts except for the copper additive (34.6% yield of CO). (ii) The CO_2 conversions are roughly lower (13.0%–28.9% against 17.0%–54.5% for the CO_2-reforming reaction) except for the iron additive which leads clearly to higher activity (15.3%–25.7% against 1.6%–5.1% for the CO_2-reforming reaction). (iii) The carbon balance indicates lower coke deposition (0.85–1.0 against 0.70–0.98 for the CO_2-reforming reaction) except also for the iron additive with which higher carbon amounts seem to be deposited (the carbon balance is 0.87–0.96 against 0.96–0.98 for the CO_2-reforming reaction).

The above results may indicate that the contribution of the CO_2/H_2 reaction to the whole CO_2 methane reforming process is less important than expected, at least for the iron additive. Coking is probably the most important secondary reaction of this process.

4. Conclusions

The presented results show that the order of activity in the methane CO_2-reforming on modified Ni/α-Al_2O_3 catalysts is Ni, Ni–Co, Ni–Ce > Ni–Cu ≫ Ni–Fe. The effect of the metal additives is attributed to their interaction with the nickel supported active phase. The catalytic performances depend also on the CO_2/CH_4 ratio and on the reaction temperature. The replacement of CH_4 by H_2 in the precedent reaction leads sensibly to lower CO_2 conversions and no effect of the metal additives is observed on the catalysts activity. It seems, thus, that the contribution of the reverse gas shift reaction in the overall process of the CO_2-reforming of methane is less important than expected.

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