Available online at www.sciencedirect.com

ScienceDirect

Catalysis Today 118 (2006) 425–432

CATALYSIS TODAY

www.elsevier.com/locate/cattod

Effect of niobium addition to Co/γ-Al_2O_3 catalyst on methane combustion

F.E. Trigueiro [a,*], C.M. Ferreira [b], J.-C. Volta [c], W.A. Gonzalez [a], P.G. Pries de Oliveria [b]

[a] *Departamento de Química, Instituto Militar de Engenharia, Praça General Tibúrcio, 80, Praia Vermelha, CEP 22290-270, Rio de Janeiro, Brazil*
[b] *Laboratório de Catálise, Instituto Nacional de Tecnologia, Av. Venezuela, 82, Praça Mauá, CEP 20081-310, Rio de Janeiro, Brazil*
[c] *Institut de Recherches sur la Catalyse/CNRS, 2 Avenue A. Einstein, F-69626 Villeurbanne Cédex, France*

Abstract

In this work, the effect of niobium addition on textural, structural, acidic, and catalytic properties of Co/γ-Al_2O_3 catalysts for use in the total combustion of methane was studied. The catalysts were prepared by using the sol–gel technique and characterized by X-ray diffraction (XRD), infrared spectroscopy of adsorbed pyridine (IR), nitrogen adsorption (BET surface area), ultraviolet–visible diffuse reflectance spectroscopy (UV–vis DRS), transmission electron microscopy in conjunction with energy-dispersive X-ray analysis (STEM–EDX), and activity in the total oxidation of methane. Results show that all cobalt-containing catalysts, regardless of the type of support, decrease the *light off* temperature of methane compared to pure γ-Al_2O_3. Therefore, the addition of 1.0% (by weight) of niobium to cobalt-containing alumina catalysts promoted a negative effect on the catalytic activity. Both cobalt-containing catalysts (4.5 and 9.3%, by weight, of Co) show a higher catalytic activity when compared to cobalt-containing niobia–alumina catalyst (6.3%, by weight, of Co). The lower activity of the niobia-containing catalysts may be associated to their acidic and textural properties.

Keywords: Catalytic combustion; Methane; Sol–gel; Niobia; Cobalt; Niobia–alumina

1. Introduction

The catalytic combustion of natural gas is considered an environment-friendly alternative to energy production due to its ability of efficient burning of lean fuel–air mixtures with low emission of harmful pollutants, such as CO, NOx or unburned hydrocarbons [1]. However, the high temperature of the gas turbines requires the use of thermally stable catalysts, which is a true limitation to the application of this clean technology.

Noble metal catalysts have been the focus of several studies on catalytic combustion. Indeed, these materials have the ability to initiate the catalytic oxidation of hydrocarbons at lower temperatures when compared to metal-oxide catalysts. By contrast, metal-oxide catalysts are relatively inexpensive, hence, much more attractive from an economic point of view.

Among the transition metals oxides, the Co_3O_4 is considered to be the most active for methane oxidation but it sinters at high temperatures [2]. This sintering process may be avoided or at least retarded by the stabilization of cobalt ions in a proper support material. γ-Al_2O_3, a commonly used support material, tends to loose its high surface area under severe temperature conditions (i.e., 1000 °C or higher), mainly due to the phase transition to α-Al_2O_3. Therefore, the inhibition of this phase transition may be achieved by the introduction of stabilizing ions [3].

Nowadays, it is well-established that the addition of niobium to catalysts promotes positive changes in their properties, either by means of an increase on acidity and/or stability, or through a synergistic effect [4]. Although some studies involving $Nb_2O_5{\cdot}Al_2O_3$ mixed-oxides have been published [5,6], none was strictly directed to their use as support materials for cobalt active phase in catalysts for the combustion of methane.

In this paper we studied the effect of niobium addition to alumina supported cobalt catalyst on the methane combustion reaction. The $Co/Nb_2O_5{\cdot}Al_2O_3$ (CoNbAl; 6.5% w/w of Co, 1.3% w/w of Nb), $Nb_2O_5{\cdot}Al_2O_3$ (NbAl; 1.1% w/w of Nb) and Co/Al_2O_3 (CoAl; 4.5 and 9.3% w/w of Co) catalysts were prepared in a one step procedure by using the sol–gel technique, which provides a material with well-defined pore size distribution, large surface area and enhanced thermal stability. Catalysts properties were studied by X-ray diffraction (XRD), infrared spectroscopy of adsorbed pyridine (IR), nitrogen

---

[*] Corresponding author.
E-mail address: ftrig@terra.com.br (F.E. Trigueiro).

0920-5861/$ – see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.cattod.2006.07.030

adsorption (BET surface area), ultraviolet–visible diffuse reflectance spectroscopy (UV–vis DRS), transmission electron microscopy in conjunction with energy-dispersive X-ray analysis (STEM–EDX), and activity in the total oxidation of methane.

2. Experimental

2.1. Catalysts preparation

All chemicals used in the experiments were analytical grade.

$Nb_2O_5{\cdot}Al_2O_3$ and γ-Al_2O_3 catalysts were prepared by the sol–gel technique from aluminum tri-*sec*-butoxide precursor—ASB (*Aldrich*).

ASB hydrolysis was carried out in *sec*-butyl alcohol (*Merck*; alcohol/ASB molar ratio ≅ 50) and distilled water (water/ASB molar ratio ≅ 30), at 90 °C, under stirring, in an acidic pH medium (near 1.0) controlled by HNO_3 addition (*Merck*). In the case of $Nb_2O_5{\cdot}Al_2O_3$ catalysts, niobium ethoxide—NE (*Aldrich*) and complexing agent acetylacetone—ACAC (*RP*) were also added, considering the following molar ratios: ACAC/NE = 1 and NE/ASB = 0.004, approximately. A transparent sol was obtained and kept under stirring for 15 min, at 90 °C, and then cooled to room temperature, while stirring for another 2 h. For Co/$Nb_2O_5{\cdot}Al_2O_3$ catalyst, $Co(NO_3)_2{\cdot}6H_2O$ was added into the sol. Then, a clear gel was obtained and allowed to age at room temperature for 21 days. The solvent was removed by liofilization technique and the liofilized material was calcined in air at 550 °C (heating rate = 5 °C/min), for 4 h.

Co/γ-Al_2O_3 catalysts were prepared by sol–gel technique from aluminum isopropoxide—AIP (*Aldrich*). AIP hydrolysis was carried out in a water/AIP molar ratio = 100, approximately, under stirring for 30 min, at 90 °C. A clear sol was obtained after 5 M HNO_3 addition (*Merck*, pH near 1.0). Then, $Co(NO_3)_2{\cdot}6H_2O$ salt was added into the sol, while stirring for another 2.5 h at 90 °C. A gel was obtained after NH_4OH (*Vetec*) addition, which was allowed to age for 7 days at room temperature. The aged gel was dried in an electric oven at 110 °C for 24 h and calcined at 550 °C (heating rate = 5 °C/min) for 2 h.

The standard Co_3O_4 was prepared by calcination of $Co(NO_3)_2{\cdot}6H_2O$ at 500 °C (heating rate = 5 °C/min) for 6 h.

2.2. Characterization

The cobalt and niobium concentrations of the catalysts were determined by gravimetric analysis.

Specific surface area of the samples was determined by the Brunauer–Emmett–Teller (BET) method from N_2 adsorption data, using a Micromeritics ASAP equipment, model 2010.

A Phillips X'Pert PRO diffractometer instrument with Cu Kα radiation = 1.54 Å (40 kV, 30 mA) was used for the X-ray diffraction (XRD) measurements. A continuous scan mode was used to collect 2θ data from 10° to 80° with a 0.05°/s scanning rate.

Transmission electron microscopy in conjunction with energy-dispersive X-ray analysis (STEM–EDX) was performed using an EDX–STEM JEOL JSM-840/A apparatus.

The acidic properties of the catalysts were studied by infrared spectroscopy of adsorbed pyridine using a FTIR spectrometer manufactured by Nicolet (Magna 560 model). First, wafers of the catalysts diluted in α-Al_2O_3 (1:1) were evacuated at 200 °C for 2 h under vacuum of 10^{-7} Torr. Then, pyridine adsorption was carried out at room temperature (25 °C) for 15 min under vacuum of 10 Torr. After the evacuation at 25 and 200 °C for 1 h (10^{-7} Torr), the spectra of adsorbed pyridine were recorded at room temperature.

Diffuse reflectance spectra were recorded in the range of 200–800 nm using an UV–vis spectrophotometer (Cary 500-8.01, *Varian*). γ-Al_2O_3 was used as reference for Nb_2O_5/Al_2O_3, Co/$Nb_2O_5{\cdot}Al_2O_3$ and Co/γ-Al_2O_3 samples. For the cobalt oxide sample, barium sulphate was the reference material.

2.3. Catalyst testing

Catalytic combustion of methane was carried out using a U-tube quartz reactor in a fixed-bed continuous-flow system at atmospheric pressure. Samples of catalysts (200 mg) mixed with a SiC (800 mg) diluent were used for each test. A gas mixture composition of 2.5% of CH_4 and 10% of O_2 balanced with N_2 was employed. Reactions were carried out within the temperature range of 300–850 °C, keeping a constant rate of 100 mL/min. Reagents and products were analyzed by an on-line gas chromatograph (Agilent 6890A model), using a thermal conductivity detector (TCD) and two serial columns (Porapak and molecular sieve). For unsupported cobalt oxide, the ratio catalyst/SiC diluent was 1:9 (100 mg of catalyst), keeping the other conditions.

3. Results and discussion

3.1. Textural properties

Table 1 shows the data obtained for chemical composition and specific surface area of the studied catalysts. As can be seen, unsupported cobalt oxide catalyst prepared by calcination of $Co(NO_3){\cdot}6H_2O$ salt showed the lowest surface area (5 m^2/g). However, all catalysts prepared by the sol–gel technique exhibit high surface area, which varied between 274 and 322 m^2/g. The NbAl mixed catalyst showed approximately the same surface area of pure γ-Al_2O_3 (322 and

Table 1
Chemical composition and specific surface area (BET) of the catalysts

Sample	% Co (by weight)	% Nb (by weight)	BET surface area ($m^2\,g^{-1}$)	Color
γ-Al_2O_3	–	–	311	White
CoNbAl	6.58	1.32	274	Dark green
NbAl	–	1.10	322	White
CoAl4	4.51	–	191	Black
CoAl9	9.24	–	213	Black
Co_3O_4	–	–	5	Black

CoNbAl, NbAl, CoAl4, and CoAl9 abbreviations correspond to Co/$Nb_2O_5{\cdot}Al_2O_3$, $Nb_2O_5{\cdot}Al_2O_3$, and Co/γ-Al_2O_3 (4.51% and 9.24% of Co) samples, respectively.

311 m^2/g, respectively), even with the presence of niobium. On the other hand, the addition of cobalt ions to the NbAl mixed oxide (CoNbAl) promoted a decrease in surface area (274 m^2/g), which is probably related to the presence of cobalt phases.

Among the catalysts prepared by sol–gel technique, CoAl4 and CoAl9 materials presented the lowest specific surface area (191 and 213 m^2/g, respectively). These results could be probably associated to differences in the preparation method, mainly the way of removing the solvent after gelification (drying step). The γ-Al_2O_3, NbAl and CoNbAl catalysts were all prepared in alcoholic medium and the solvent (*sec*-butyl alcohol) was extracted by using the liofilization technique. By contrast, CoAl4 and CoAl9 catalysts were prepared in aqueous medium and the solvent (water) was eliminated by direct heating the aged gel in an electric oven (110 °C/24 h). In the latter case, the high surface tension of water might have caused some shrinking of the gel during the drying step (liquid–vapor interface), thus producing a catalyst material with a lower surface area. However, when the gel was dried by using the liofilization technique, the final catalyst showed a higher surface area. Here, the formation of an interface liquid–vapor is not observed since this technique involves the passage of the solvent from the solid to the vapor state (sublimation), avoiding or, at least, minimizing the collapse of the catalyst structure.

Although CoAl4 and CoAl9 catalysts have been prepared by using the same method, it is not possible to establish a direct correlation between the cobalt content and the specific surface area of both materials. In fact, each catalyst was obtained by an individual sol–gel preparation and, differently from those that are prepared via impregnation method, these solids were not derived from the same source of alumina.

3.2. Structural properties

3.2.1. X-ray diffraction

Fig. 1 presents XRD patterns of the pure alumina (Al), NbAl, CoNbAl, CoAl4, CoAl9, and unsupported cobalt oxide (Co) catalysts. The XRD pattern of unsupported cobalt oxide shows relatively high diffraction intensities of the spinel phase of Co_3O_4 (main diffraction line at 37°—(3 1 1) plane). The XRD pattern of pure alumina reveals a partially amorphous material having the characteristic structure of γ-alumina.

The XRD patterns of CoAl4 and CoAl9 catalysts show an intense signal in $2\theta = 37°$, which tends to increase as the cobalt content increases. Other signals in $2\theta = 19°$, 32°, and 59°, approximately, can also be observed. These results suggest that the cobalt phases present in the cobalt-containing alumina catalysts have a spinel structure, which could be assigned to Co_3O_4 and/or $CoAl_2O_4$ phases. However, due to the structural similarity of these two phases, it is not possible to distinguish between one spinel phase and the other based on XRD data only [7,8]. No signals corresponding to cobalt monoxide phase (CoO) were detected by XRD analysis.

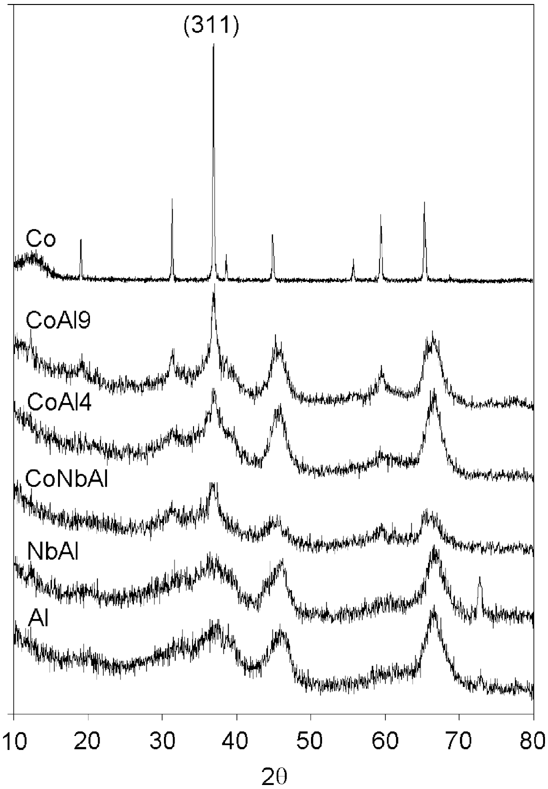

Fig. 1. XRD patterns of γ-Al_2O_3 (Al), NbAl, CoNbAl, CoAl4, CoAl9, and unsupported cobalt oxide (Co) catalysts.

The XRD patterns of $Nb_2O_5{\cdot}Al_2O_3$ mixed oxide (near 1.0%, by weight, of Nb) and γ-Al_2O_3 catalysts are quite similar. Indeed, no signals assigned to niobium phases were detected in the diffractogram of NbAl catalyst. In the XRD pattern of the cobalt-containing niobia–alumina catalyst (CoNbAl), it is noted a peak in $2\theta = 37°$, which indicates the presence of cobalt phases with a spinel structure, such as Co_3O_4 and/or $CoAl_2O_4$. Also, signals assigned to niobium compounds were not detected.

3.2.2. Diffuse reflectance UV–visible spectroscopy (UV–vis DRS)

Fig. 2 presents UV–vis DRS spectra of the studied catalysts. For all samples, species of cobalt in octahedral and tetrahedral coordination were detected. As can be seen, the spectrum of unsupported cobalt catalyst (Co) is characterized by two broad bands at 380 and 710 nm, and a shoulder at 450 nm. According to the literature [9,10], the absorption bands at 380 and 710 nm are assigned to the spinel structure of Co_3O_4 (represented by $Co^{2+}Co_2{}^{3+}O_4$), which is constituted by Co(II) and Co(III) ions in tetrahedral and octahedral coordinations, respectively. The shoulder at 450 nm is an indication of the existence of Co(II) species in octahedral coordination, similar to those of CoO structure. Also, the formation of a pre-spinel structure containing Co(II) ions in octahedral coordination may not be discharged.

UV–vis DRS spectra of Co/γ-Al_2O_3 (CoAl4 and CoAl9) catalysts present a band near 380 nm and three bands at 542, 578 and 624 nm, characteristic of the presence of Co(II) in tetrahedral coordination, as found in the spinel structure of $CoAl_2O_4$ [9].

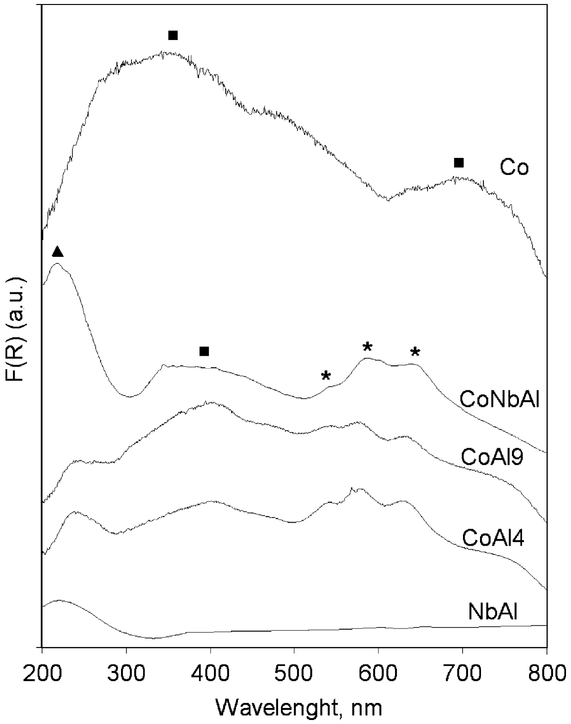

Fig. 2. UV–vis DRS spectra of the NbAl, CoNbAl, CoAl4, CoAl9, and unsupported cobalt oxide (Co) catalysts. Symbols: (■) Co_3O_4 spinel; (★) $CoAl_2O_4$ spinel; (▲) metal–ligand charge transfer.

In the spectra of both niobium-containing catalysts (NbAl and CoNbAl), it is noted an intense band at 215 nm, usually assigned to metal–ligand charge transfer. The spectrum of CoNbAl catalyst also presents bands at 380 nm, attributed to Co(III) species in octahedral coordination (Co_3O_4 spinel), and at 536, 582, and 635 nm, characteristic of Co(II) species in tetrahedral coordination ($CoAl_2O_4$ spinel).

3.3. Acidic properties

Fig. 3 shows the infrared spectra of adsorbed pyridine in the wave number range of 1700–1400 cm^{-1}, where bands due to skeletal vibrations of the pyridinic ring can be observed. As can be noted, the spectra of all catalysts present bands at 1444, 1489, 1575, 1591, and 1612 cm^{-1}, characteristic of pyridinium ions ($C_5H_6N^+$) coordinately bonded to Lewis acid sites (LAS) [6]. However, the most characteristically band related to pyridine adsorbed on Brönsted acid sites (BAS) that frequently occurs near 1545 cm^{-1} was not observed neither in the spectra of Al_2O_3-based catalysts, nor in the $Nb_2O_5{\cdot}Al_2O_3$-based catalysts. Apparently, the addition of only 1.0%, by weight, of niobium to alumina-based catalysts was not sufficient to create BAS. Indeed, literature reports the creation of BAS on $Nb_2O_5{\cdot}Al_2O_3$ samples with higher niobium oxide content [11,12,13].

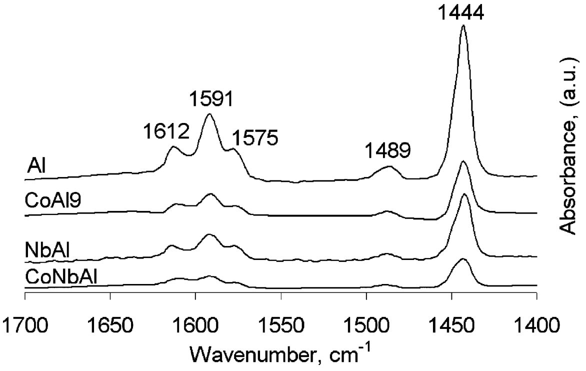

Fig. 3. Infrared spectra of adsorbed pyridine in the wave number range 1400–1800 cm^{-1} for γ-Al_2O_3, CoAl9, NbAl, and CoNbAl catalysts.

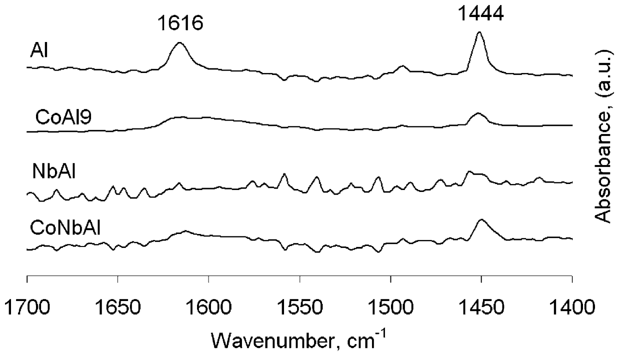

Fig. 4. Infrared spectra of adsorbed pyridine in the wave number range 1400–1800 cm^{-1} for γ-Al_2O_3, CoAl9, NbAl, and CoNbAl catalysts after desorption at 200 °C.

Fig. 4 shows the evolution of the bands associated to pyridinium ions bonded to LAS after desorption at 200 °C. For γ-Al_2O_3 catalyst, the intensity of the bands near 1444 and 1612 cm^{-1} significantly decreased, and the bands at 1489, 1575 and 1591 cm^{-1} totally disappeared after desorption. Only a small band at 1444 cm^{-1} and a broad band of very low intensity between 1570 and 1620 cm^{-1} can be observed in the spectra of CoAl9 sample. For CoNbAl catalyst, only the band at 1444 cm^{-1} still appears after desorption at 200 °C, but in a very low intensity. No bands related to the interaction of pyridine with LAS were detected for NbAl catalyst.

In fact, the acidic behavior observed after pyridine desorption at 200 °C allows a preliminary evaluation of the strength of catalysts LAS. The results showed in Fig. 4 indicate that γ-Al_2O_3 presents the strongest acidic sites when compared to CoAl9, CoNbAl and NbAl catalysts. On the other hand, NbAl catalyst presents the weakest LAS among all studied catalysts.

3.4. Total combustion of methane

Although the unsupported cobalt catalyst (Co_3O_4 spinel) presents a high activity for methane oxidation, this material is thermally unstable and tends to deactivate during the reaction of methane combustion even at temperatures as low as 500 °C (Fig. 5). In fact, methane conversion over unsupported cobalt catalyst drops from 75 to 68%, approximately, after only 7 h of reaction time at this relatively low temperature. By contrast, an enhancement on thermal stability is observed when cobalt phase is dispersed in a support material. For instance, the

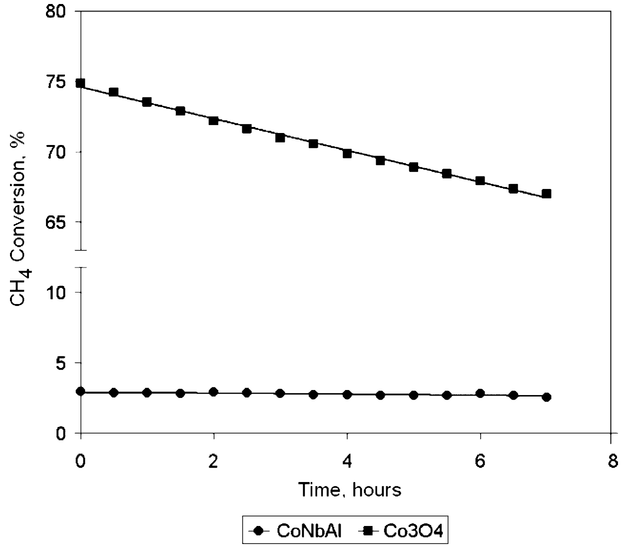

Fig. 5. Stability test of unsupported cobalt oxide (Co_3O_4) and CoNbAl catalysts at 500 °C.

activity of CoNbAl catalyst remained unchanged at the same reaction conditions. On the other hand, this catalyst shows a lower activity in relation to unsupported cobalt oxide, despite having a higher surface area. Similar results were also obtained for the cobalt-containing alumina catalysts (CoAl4 and CoAl9).

Fig. 6 shows the curves of methane conversion on sol–gel prepared catalysts (γ-Al_2O_3, NbAl, CoNbAl, CoAl4, and CoAl9). All cobalt-containing catalysts, independently of the support material, diminish the light off temperature of methane combustion in relation to pure γ-alumina ($T_{\text{light off}} > 600$ °C). The addition of 1.0%, by weight, of niobium did not change the light off temperature of the γ-Al_2O_3. However, a behavior somewhat distinct is observed at higher temperatures. In fact, the NbAl catalyst shows a lower activity than pure γ-Al_2O_3 at temperatures above 700 °C, which could be an indication that a negative interaction between niobium and alumina is probably taking place at high temperature conditions.

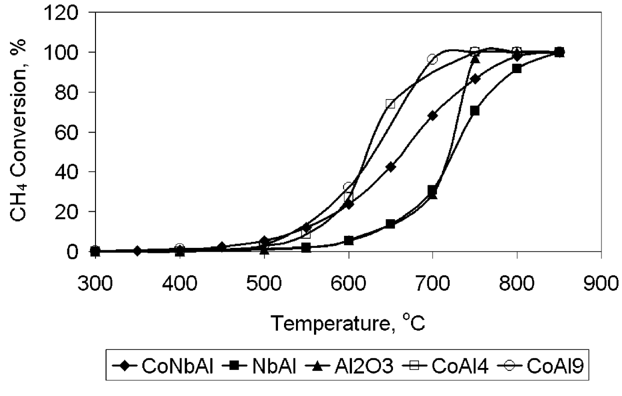

Fig. 6. Methane conversion over CoAl4, CoAl9, CoNbAl, NbAl, and γ-Al_2O_3 catalysts.

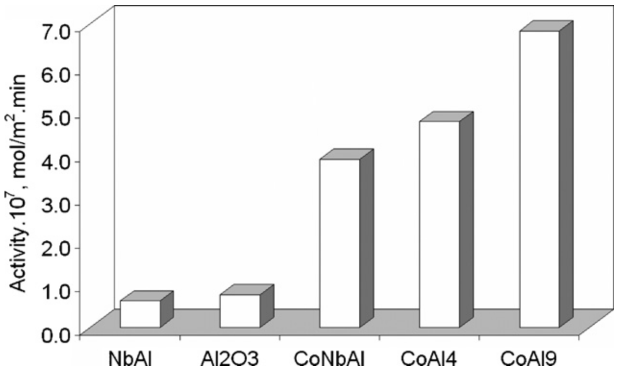

Fig. 7. Catalytic activity in the complete oxidation of methane at 550 °C over CoAl4, CoAl9, CoNbAl, NbAl, and γ-Al_2O_3 catalysts.

The effect of niobium addition to the alumina-based catalysts is better seen in Fig. 7, which shows a comparison between the specific activities of the studied catalysts (mol/m^2 min) considering only the data collected at 550 °C (conversion level below 10%). It is clear that the introduction of 1.0%, by weight, of niobium to γ-Al_2O_3 promotes a decrease in catalytic activity. A similar negative effect is also observed for the CoNbAl catalyst. In fact, both cobalt-containing alumina catalysts (CoAl4 and CoAl9) exhibit higher activities on the methane combustion reaction when compared to CoNbAl catalyst. Also, it is important to notice that CoAl4 (4.5%, by weight, of Co) catalyst presents a higher specific activity than CoNbAl catalyst (6.6%, by weight, of Co) in spite of its lower cobalt content.

The lower activity of the niobia-containing alumina catalysts may be related to their acidic properties. Although niobia is considered a strong acid catalyst, the addition of 1.0%, by weight, of niobium to alumina was not sufficient to create new and stronger acid sites. In fact, the acid sites of both niobia-containing catalysts are weaker than those observed in the alumina-based catalysts (Fig. 4). According to Xiao et al. [16], the acidity character of the oxide material is the prevailing factor in influencing the catalyst performance. Higher activities in the reaction of methane combustion were found for the more acidic catalysts, despite of their worse oxygen mobility and conductivity properties.

According to Datka et al. [11], the addition of niobium to alumina would create Nb–OH–Al bonds associated to Brönsted acid sites in $Nb_2O_5 \cdot Al_2O_3$ systems. The acidic character of these new bridging hydroxyl groups tends to increase as the number of Nb atoms located around the Nb atom of the bridging group also increases. However, bands associated to pyridine adsorbed on Brönsted acid sites were only observed in niobia–alumina mixed samples containing more than 1.0%, by weight, of niobium [11,12,13]. In our work, no bands associated to Brönsted acid sites were detected in the infrared spectra of pyridine adsorbed on the niobia-containing catalysts. Perhaps, the Brönsted acid sites generated after the niobium addition are not strong enough to interact with pyridine molecule, and so, could not be detected by this technique.

The lower activity of the niobia-containing alumina catalysts may also be related to their textural properties, mainly to the homogeneity of the cobalt and niobium distribution on alumina

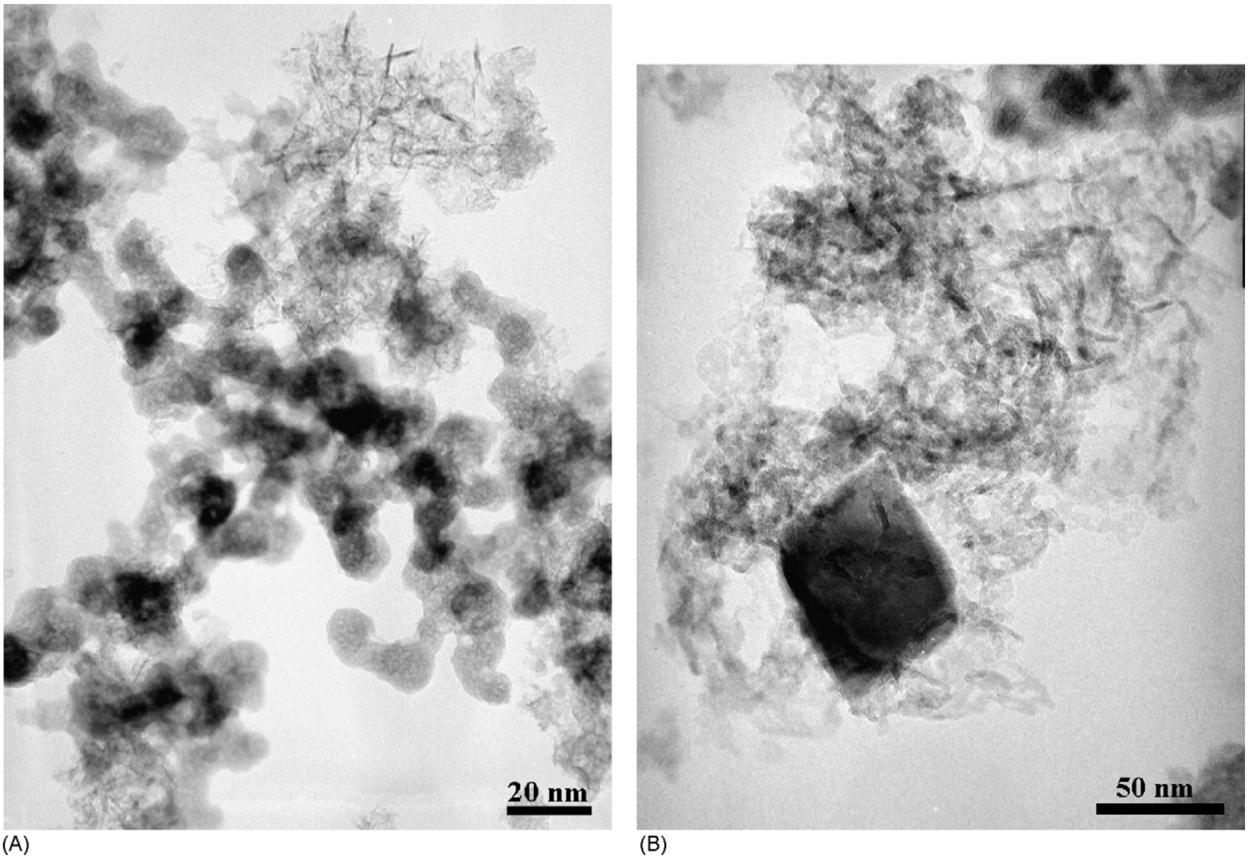

Fig. 8. (A) STEM images of the CoNbAl catalyst. Isolated regions rich in alumina (needle-like particles) and niobia with homogeneously distributed cobalt element (round-shaped particles) and (B) STEM images of the CoNbAl catalyst. Region rich in alumina (needle-like particles) containing an isolated particle of cobalt oxide (particle diameter of 50 nm, approximately).

material. Figs. 8 and 9 show the STEM images of CoNbAl and NbAl catalysts, respectively. Table 2 shows the elemental composition of both niobia-containing alumina samples obtained by EDX analysis.

As can be seen, the EDX–STEM results indicate that both NbAl and CoNbAl catalysts are constituted by a non-homogeneous material, containing isolated regions of niobia (round-shaped particles) and γ-alumina (needle-like particles). Furthermore, cobalt particles are differently distributed in niobia and alumina materials. Fig. 8(A) clearly shows well-dispersed cobalt particles on the niobia material, whereas larger and highly isolated cobalt particles can be noted on the alumina region of the non-homogeneous CoNbAl catalyst (Fig. 8(B)). The average diameter of cobalt particles when distributed in the alumina material is 50 nm, approximately. On the other hand, the cobalt particles have an average diameter five times smaller when distributed in the niobia material (near 10 nm).

Table 2
Elemental composition of NbAl and CoNbAl catalysts by EDX

Sample	Figure	Element (%)				
		O	Al	K	Co	Nb
NbAl	9	41.5	28.3	1.1	–	28.6
CoNbAl	8(A)	43.2	33.7	1.1	3.6	18.4
	8(B)	30.0	10.6	–	59.8	0.0[a]

[a] Less than squared sigma.

It seems that cobalt active phase is preferentially distributed in the niobia region of the heterogeneous CoNbAl catalyst. By contrast, in cobalt-containing alumina catalysts, cobalt active phase is only dispersed in alumina material, which has a higher surface area. Consequently, both CoAl catalysts are more active in the reaction of methane combustion than CoNbAl catalyst.

In fact, the preparation of highly homogeneous mixed oxides by sol–gel technique is complex and involves the control of a series of experimental parameters. For sol–gel mixed materials that are prepared from metallic alkoxide precursors having different reactivities, such as aluminum tri-*sec*-butoxide and niobium ethoxide, the probability of obtaining a heterogeneous material is really high. In these cases, it is well-recognized that the use of complexing agents enables the adjustment of the relative reactivities of the metallic alcoxide precursors in such a way that they have similar rates of hydrolysis and/or polymerization [14]. Although acetylacetone has been used in our sol–gel preparations in order to control the hydrolysis step of niobium ethoxide, it can be noted from the EDX–STEM results that the presence of this complexing agent was not sufficient to control the hydrolysis rate of both precursors, and niobium ethoxide still reacted much faster than aluminum tri-*sec*-butoxide. As a result, non-homogeneous catalysts containing isolated regions of niobia and alumina were obtained.

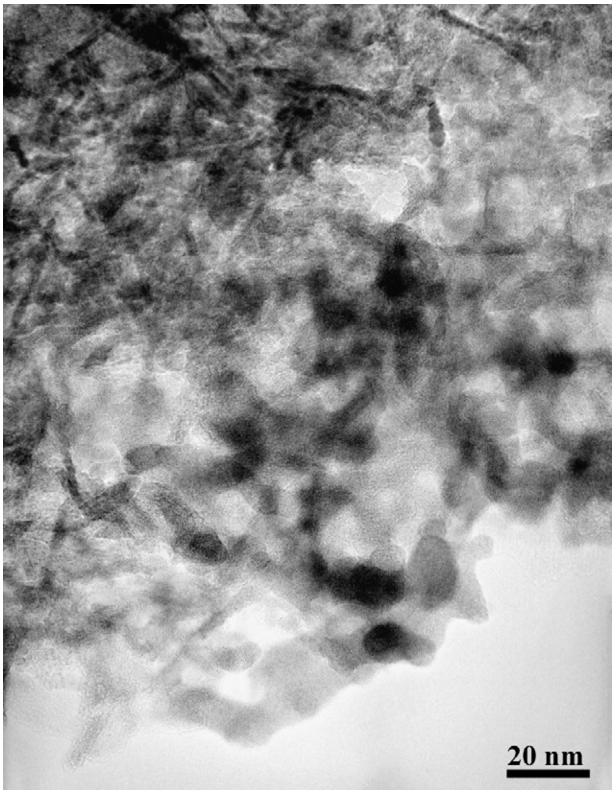

Fig. 9. STEM image of the NbAl catalyst. Region containing both alumina (needle-like particles) and niobia (round-shaped particles) in similar proportions.

The heterogeneity of the niobia-containing alumina materials may also play an important role in the performance of the catalysts in the reaction of methane combustion at higher temperatures. As previously discussed, the conversion of methane over both NbAl and CoNbAl catalysts drops at temperatures higher than 700 °C, reaching values lower than the observed for pure alumina or cobalt-containing alumina catalysts (Fig. 6). This decrease in the catalytic activity of the niobium-containing samples is probably associated with the separate crystallization of Nb_2O_5 *TT* compound at high temperature conditions [15], which may be facilitated by the heterogeneous character of these samples.

On the other hand, cobalt-containing alumina catalysts show a completely different catalytic behavior. At 700 °C, both CoAl4 and CoAl9 catalysts are more active in the reaction of methane oxidation when compared to the niobia-containing alumina catalysts (Fig. 6). Moreover, the catalytic activity of the cobalt-containing alumina samples tend to increase with increasing cobalt content. While the total combustion of methane is achieved when the reaction is carried out over the CoAl9 catalyst at 700 °C, nearly 5% of methane still remains unreacted when CoAl4 sample is used as the combustion catalyst at the same reaction conditions. When compared to the pure alumina catalyst, the cobalt-containing alumina catalysts are much more active, which confirms that the cobalt species are active components for methane combustion.

The better performance of the CoAl9 sample is probably associated with the nature and the quantity of the cobalt species present in this catalyst. As indicated by UV–vis DRS (Fig. 2) and XRD (Fig. 1) analysis, both CoAl4 and CoAl9 catalysts are constituted by $CoAl_2O_4$ and Co_3O_4 spinel compounds. The formation of $CoAl_2O_4$ spinel is facilitated by the sol–gel technique, considering the fact that cobalt ions are directly added to the alumina sol and are present in the reaction medium during the building of the alumina lattice (gelation step). In other words, the creation of Al–O–Co bonds during the gelation process is expected to occur, which finally leads to the formation of the $CoAl_2O_4$ compound. As a matter of fact, part of the added cobalt ions does not interact with the aluminum cations and is transformed to Co_3O_4 spinel after calcination at 550 °C. According to literature data, the catalytic activity of $CoAl_2O_4$ and Co_3O_4 compounds are quite different. While Co_3O_4 compound catalyzes the combustion of hydrocarbons, $CoAl_2O_4$ compound is inactive [9]. Due to its higher cobalt content, a higher quantity of Co_3O_4 active phase is available in the CoAl9 sample for methane oxidation reaction when compared to the CoAl4 sample. This could explain the higher activity of CoAl9 sample if we consider the high activity of Co_3O_4 compound in the oxidation of hydrocarbons [9,10,16,17].

4. Conclusions

The cobalt-containing alumina and niobia–alumina catalysts prepared by sol–gel method are active in the methane combustion. The cobalt-containing alumina catalysts are more active than cobalt-containing niobia–alumina catalyst. Moreover, the activity of these catalysts increases with cobalt content, which is probably related to an increase in the quantity of the Co_3O_4 active phase. Although the unsupported cobalt catalyst (Co_3O_4 spinel) presents a high activity for methane oxidation, this material is thermally unstable and tends to deactivate during the reaction of methane combustion even at temperatures as low as 500 °C.

The lower activity of the niobia-containing catalysts may be associated to their acidic and textural properties. Although the niobia compound itself is considered a strong acid catalyst, the addition of 1.0%, by weight, of niobium to alumina is not sufficient to create new and stronger acid sites. The acid sites of the niobia-containing catalysts are weaker than those observed in the alumina-based catalysts. Also, the niobia-containing catalysts are constituted by non-homogeneous materials, containing isolated regions of niobia and alumina. The EDX–STEM results show well-dispersed cobalt particles on the niobia region, whereas larger and highly isolated cobalt particles can be noted on the alumina region of the heterogeneous cobalt-containing niobia–alumina catalyst.

At temperatures higher than 700 °C, the conversion of methane over the niobia-containing alumina catalysts drops drastically, reaching lower values than the observed for the pure alumina catalyst. This negative behavior is probably associated with the separate crystallization of Nb_2O_5 *TT* compound at high temperature conditions, which may be facilitated by the heterogeneous character of the niobia-containing samples.

Acknowledgements

The authors thank to IME and INT for the financial and technical assistance, and IRC-CNRS for the EDX–STEM analysis.

References

[1] R.A. Dalla-Betta, Catal. Today 35 (1997) 129.

[2] M.F.M. Zwinkels, S.G. Jarås, P.G. Menon, T.A. Griffin, Catal. Rev. Sci. Eng. 35 (1993) 319.

[3] D.L. Trimm, Catal. Today 26 (1995) 231.

[4] M. Ziolek, Catal. Today 78 (2003) 47.

[5] A.L. Petre, J.A. Perdigón-Melón, A. Gervasini, A. Auroux, Catal. Today 78 (2003) 377.

[6] C.L.T. da Silva, V.L.L. Camorim, J.L. Zotin, M.L.R.D. Pereira, A.C. Faro Jr., Catal. Today 57 (2000) 209.

[7] B. Jongsomjit, J. Panpranot, J.G. Goodwin Jr., J. Catal. 204 (2001) 98.

[8] L. Ji, J. Lin, H.C. Zeng, J. Phys. Chem. B 104 (2000) 1783.

[9] J.Y. Yan, M.C. Kung, W.M.H. Sachtler, H.H. Kung, J. Catal. 172 (1997) 178.

[10] L.F. Liotta, G. Pantaleo, A. Macaluso, G. Di Carlo, G. Deganello, Appl. Catal. A 245 (2003) 167.

[11] J. Datka, A. Turek, J.M. Jehng, I.E. Wachs, J. Catal. 135 (1992) 186.

[12] J.H. Jehng, I.E. Wachs, Catal. Today 8 (1990) 37.

[13] F.M.T. Mendes, C.A. Perez, R.R. Soares, F.B. Noronha, M. Schmal, Catal. Today 78 (2003) 449.

[14] A.J. Lecloux, J.P. Pirard, J. Non-Cryst. Solids 225 (1998) 146.

[15] J.H. Jehng, I.E. Wachs, Catal. Today 16 (1993) 417.

[16] T.-C. Xiao, S.-F. Ji, H.-T. Wang, K.S. Coleman, M.L.H. Green, J. Mol. Catal. A 175 (2001) 111.

[17] V.G. Milt, M.A. Ulla, E.A. Lombardo, Catal. Lett. 65 (2000) 67.