Catalysis Today 176 (2011) 234–238

Contents lists available at ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

Fluidized bed plasma for pre-treatment of Co-ferrierite catalysts: An approach to NO_x abatement

R. Bartolomeu[a,b], M. Foix[b,c], A. Fernandes[a], M. Tatoulian[c], M.F. Ribeiro[a], C. Henriques[a], P. da Costa[b,*]

[a] *Instituto Superior Técnico, Institute for Biotechnology and Bioengineering, Centre for Biological and Chemical Engineering, Av. Rovisco Pais, 1049-001 Lisboa, Portugal*
[b] *Université Pierre et Marie Curie, Paris 6, Laboratoire de Réactivité de Surface - CNRS UMR 7197, 4 Place Jussieu, 75252 Paris 05, France*
[c] *École Nationale Supérieure de Chimie Paris – Chimie ParisTech, Laboratoire "Génie des Procédés Plasmas et Traitement de Surface", 11 rue P. et M. Curie, 75231 Paris Cedex 03, France*

ARTICLE INFO

Article history:
Received 18 October 2010
Received in revised form 8 December 2010
Accepted 22 December 2010
Available online 5 February 2011

Keywords:
Plasma treatment
Cobalt-based catalyst
HC-SCR
Fluidized bed
Calcination

ABSTRACT

Replacement of calcination procedures used during catalyst preparation, by a plasma treatment, was studied over a Co-ferrierite (Co-FER) catalyst. The catalyst was tested in the NO_x selective catalytic reduction reaction.

A combination of UV–Vis spectroscopy and TG analysis revealed the presence of ammonium ions on the untreated and plasma Co-FER samples but not on the calcined one. Therefore, it can be concluded that the plasma treatment was not able to replace the thermal calcination step.

The evaluation of catalyst behaviour was performed both under temperature programmed surface reaction (TPSR) and under steady-state conditions at different temperatures.

NO oxidation tests showed that, during TPSR runs, calcined catalyst produces more NO_2 than plasma catalyst. NO_x consumption during TPSR of plasma catalyst confirms that precursors used on the ion-exchange procedure are still present on the catalyst even after the plasma treatment, reacting with NO to produce R-NO_x, N_2O and N_2.

Concerning *de*NO_x tests using ethanol as reducing agent, TPSR tests showed higher NO_x conversions over untreated and plasma catalysts due to the presence of ammonium and acetate precursors on these catalysts. Untreated, plasma and calcined catalysts present the same NO_x and CO_x conversions in isothermal tests.

1. Introduction

In zeolite metal-containing catalysts, preparation usually includes thermal activation steps that aim not only to decompose metal precursors, in order to obtain the appropriate metal species, but also to stabilize those species in particular extra-framework locations [1].

The conventional preparation of dispersed catalysts usually requires a combination of several unit operations, including: (i) introduction of the metal precursor on the support using techniques such as ion-exchange, impregnation, co-precipitation, or deposition; (ii) drying; (iii) calcination and, if necessary, (iv) reduction with H_2. However, the present state-of-the-art for catalyst preparation is far from perfect [2]. Plasma treatment is one of the most popular treatments of materials. This treatment affects only the catalyst surface without changing its bulk properties. Besides, it can be used under oxidative, reductive or inert atmosphere. The use of plasmas for catalysis is now well developed [3–6] and some authors have used a plasma treatment in a low pressure system to replace the thermal calcination of the catalyst [7–9].

Depending on the operating conditions (type of the electrical discharge, power density, duration, etc.), the plasma treatment can be used for (i) surface cleaning and etching (O_2, Ar/O_2 mixtures), (ii) surface functionalisation (N_2, NH_3, O_2 plasmas), (iii) cross-linking (He, Ar plasmas). However, special attention has to be paid to the treatment of powders with diameter of a few hundreds of micrometers. Fluidized bed reactors can provide a uniform treatment and an excellent gas–solid heat transfer [9,10], leading to new catalytic properties of the prepared materials [3]. According to the literature, the plasma treatment is always used after catalyst preparation and drying [11,12].

The aim of this work is to evaluate if the thermal calcination of the Co-FER catalyst, used to decompose the precursors that remain on the catalyst after its preparation, can be replaced by a plasma treatment in a low pressure fluidized bed reactor.

---

[*] Corresponding author. Present address: Université Pierre et Marie Curie, Paris 6, Institut Jean Le Rond d'Alembert, CNRS UMR 7190, 2 Place de la Gare de Ceinture, 78210 Saint Cyr l'école, France. Tel.: +33 1 30 85 48 62; fax: +33 1 30 85 48 99.
E-mail address: patrick.da_costa@upmc.fr (P. da Costa).

0920-5861/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.cattod.2010.12.051

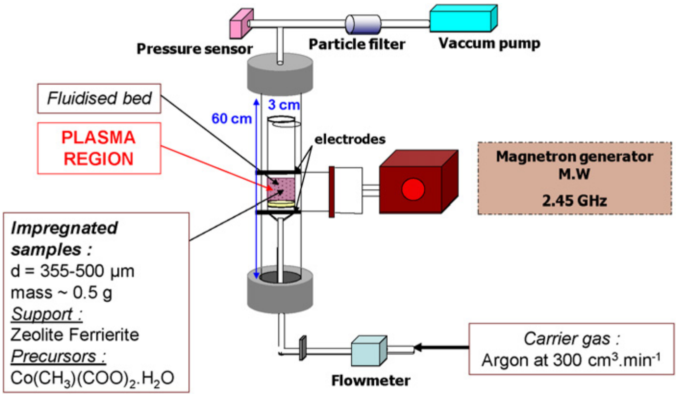

Fig. 1. Experimental set-up of the fluidized bed reactor (FBR) used in the microwave plasma surface treatment of plasma Co-FER catalyst.

The selective catalytic reduction (SCR) of nitrogen oxides with hydrocarbons is a promising technology to control NO_x emissions both from stationary and from mobile sources. Cobalt-based catalysts were used in this work since they have shown promising results when ethanol is used as a reducer agent [13]. After cobalt introduction, a low fluidized bed plasma reactor was used in order to treat the Co-FER catalysts. A comparison with "classical calcination" was performed in order to evaluate plasma treatment efficiency.

2. Experimental

2.1. Catalyst preparation and calcination

Zeolite catalysts were prepared from an alkali form of ferrierite, NaK-FER, with a Si/Al = 9 (*TOSOH Co*., Japan).

The monometallic Co-FER (3 wt.% Co) catalyst was obtained by ion-exchanging the NH_4-FER form with a $Co(CH_3COO)_2{\cdot}H_2O$ solution. The NH_4-FER form was prepared by ion-exchange at 80 °C for 3 h, three times, with a 4.0 M NH_4NO_3 solution, under strong agitation. The catalyst was then washed with distilled water and dried at 100 °C for 12 h. The NH_4-FER powders were dipped in a 0.05 M aqueous solution of $Co(CH_3)(COO)_2{\cdot}H_2O$ and strongly agitated at 80 °C for 24 h. The catalyst was then filtered and washed several times with distilled water. Finally, the catalyst was dried at 120 °C overnight, prior to the two different processes, i.e. (i) calcination in air at 500 °C for 2 h (10 °C/min) or (ii) plasma treatment in the fluidized bed reactor with microwaves.

2.2. Plasma reactor

The powder zeolite samples were pressed in order to form large pellets that were then crushed and sieved between 355 and 500 μm in order to obtain a homogeneous fluidization and to avoid the loss of powders in the pumping system.

The fluidized bed reactor (FBR) consisted of a cylindrical *Pyrex* glass tube of 30 mm internal diameter and 600 mm length, as shown in Fig. 1. The impregnated powders (density: 0.55 g cm^{-3}, mean diameter: 355–500 μm) were fluidized with Ar which passed through a porous glass plate. Gas flow rates were regulated by *MKS* mass-flow controllers. All experiments were performed at minimum fluidization velocity conditions which were previously determined from the pressure drop versus gas flow rate.

The pressure was controlled by a *Pirani*-type vacuum gauge and maintained at 0.7 mbar by a two stage *Pfeiffer* pump. To prevent powders from damaging the pump system, a dust trap was also installed. A magnetron (0–1000 W) was used in order to create a plasma microwave energy source of 500 W. A few grams of the catalyst (0.5 g) were placed into the reactor and the carrier gas was passed through the porous plate for 30 min with a flow rate of 300 cm^3 min^{-1} to ensure a good fluidization of the particles in the microwave (M.W.) plasma.

2.3. Catalyst characterisation

The catalysts chemical composition was determined by ICP analysis.

DRS (diffuse reflectance) UV–Vis spectra were carried out on a *Varian Cary 5000* UV-VIS-NIR spectrophotometer. Spectra were recorded at a medium speed, with a slit width of 2 nm. The spectra were collected at room temperature, in air, in the range of 200–2500 nm. Spectralon was used as a reference.

Thermogravimetric (TG) analyses were performed in a *Setaram TG-DSC92* thermobalance under air flow (100 mL min^{-1}) at a heating rate of 5 °C min^{-1} up to 800 °C. For each analysis, about 30 mg of sample was put in a platinum basket.

2.4. Catalytic tests

The reduction of NO by ethanol (EtOH) in the presence of oxygen excess was carried out in a fixed-bed U reactor, with 110 mg of catalyst. A gas mixture containing 250 ppm NO, 1100 ppm EtOH, 7 vol.% O_2 with Argon as balance was fed at a rate of 250 mL min^{-1}, through mass flow controllers (*Brooks 5850*). NO oxidation tests were performed with 250 ppm NO and 7 vol.% O_2. The corresponding GHSV was 45,000 h^{-1}, considering a bulk catalyst density of 0.3 g cm^{-3}.

Reactant mixture was allowed to stabilize in a reactor by-pass until its composition was stable. Then, temperature programmed surface reaction (TPSR) was carried out at a heating rate of 10 °C min^{-1} up to 500 °C. After each TPSR, isothermal conversion points were then taken between 500 °C and 250 °C, in steps of 50 °C. The temperature was maintained from 45 to 120 min at each step until gas composition was constant.

NO_x concentrations were followed by an *Eco Physics CLD 700 AL* chemiluminescence analyser while N_2O and CO_x concentrations were followed by two *Siemens Ultramat 6* infrared analysers. A *Pfeiffer Vacuum GSD 301* MS was used to follow the *m*/*z* signal 28 (N_2/CO) during NO oxidation TPSR runs.

3. Results and discussion

3.1. Catalyst characterisation

Fig. 2 shows the DRS UV–Vis spectra (200–2500 nm) of the different samples: untreated, plasma-treated and calcined Co-FER catalysts. All the samples present an intense and broad band at about 220 nm (UV region), usually attributed to oxygen to metal charge transfer bands. The Co-FER samples that were untreated (spectrum (a)) or plasma-treated (spectrum (b)) show two distinct bands at 520 (doublet, visible region) and 1250 nm (NIR region) relative to the (d–d) transitions of hydrated Co^{2+} ions in an octahedral environment [14]. The sharp bands also observed at about 1410 and 1910 nm originate, respectively, from overtone (2ν) and combination ($\nu+\delta$) bands of adsorbed water. These two samples present, in addition, two other bands in the NIR region, at about 1540 and 2110 nm, but somewhat broader: the values match well with overtone and combination bands of N–H groups [15], thus evidencing the presence of ammonium species in both samples, meaning that the plasma treatment did not decompose ammonium species present within the zeolite pores.

On the other hand, calcined catalyst (spectrum (c)) has distinct changes when compared with the other two Co-FER catalysts. Bands from hydrated Co^{2+} species seem to disappear while new

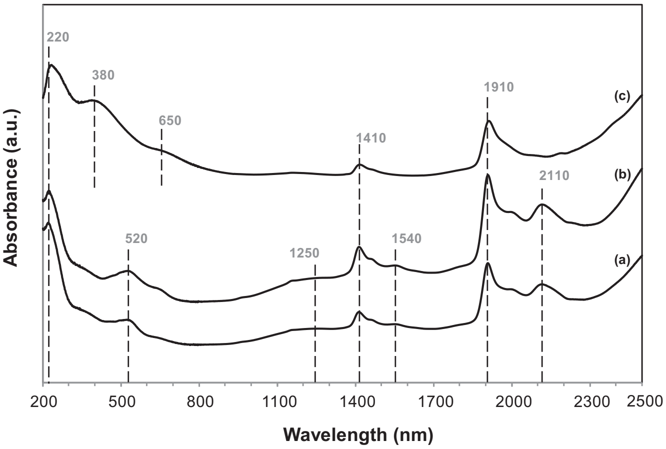

Fig. 2. DRS UV–Vis spectra at room temperature of untreated (a), plasma (b) and calcined (c) Co-FER catalysts.

bands develop at 380 and 650 nm: these bands are commonly attributed to Co oxide species with a spinel structure (Co_3O_4) [16]. Probably the former Co^{2+} species are still present but are hidden by the strong absorption of cobalt oxide species as the overall spectrum intensity increased. In fact, as no thermal treatment (in situ dehydration) has been performed on the different samples, identification of dehydrated, tetrahedral Co^{2+} species occupying the different exchange positions of the FER structure is not possible [17]. However, it should be noted that DRS UV–Vis was used to evaluate the presence of overtone and combination bands originated from N–H groups in the NIR region, in order to evaluate the existence of ammonium species in the catalysts. Therefore, no in situ treatment was done. Indeed, in the case of calcined Co-FER catalyst, no bands corresponding to NH_4^+ species are detected. In summary, one can say that, after thermal calcination, ammonium species are removed while isolated Co species evolve to polymeric (oxide) species.

TG measurements (Fig. 3) have been performed in order to compare weight losses from the different catalysts. All catalysts show a first weight loss at low temperature (100 °C) related to water desorption. Calcined Co-FER catalyst does not present additional weight loss, demonstrating the efficiency of thermal calcination to completely remove ammonia species from the catalyst. On the other hand, NH_4-FER material and Co-FER untreated and plasma catalysts present a second weight loss at about 300–500 °C corresponding to the release of NH_3. Furthermore, the Co containing samples show decomposition temperatures slightly lower than the ammonium form zeolite, probably as a consequence of the presence of cationic species Co^{2+}. Quantitative results show a higher weight loss for NH_4-FER (3.3 wt.%, dry basis) while Co-based samples present similar values (2.2 wt.%), which is not surprising as ion exchange occurred and NH_4^+ content is expected to be lower. The similarity between untreated and plasma Co-FER catalysts seems to demonstrate, again, the relative low effect of plasma treatment on NH_4^+ species decomposition.

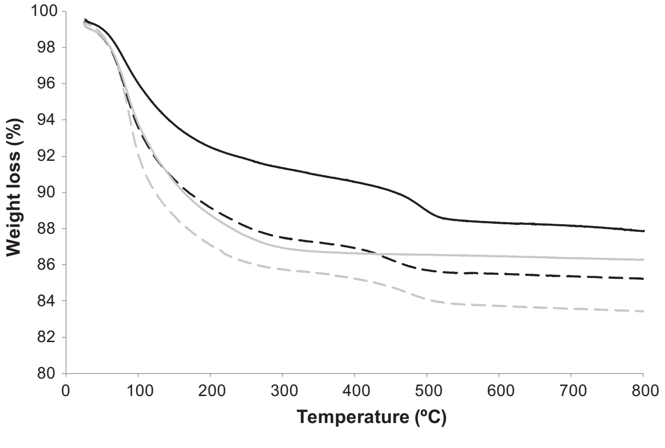

Fig. 3. TG profiles of untreated (—) NH_4-FER; untreated (– –), plasma (**– –**) and calcined (—) Co-FER catalysts.

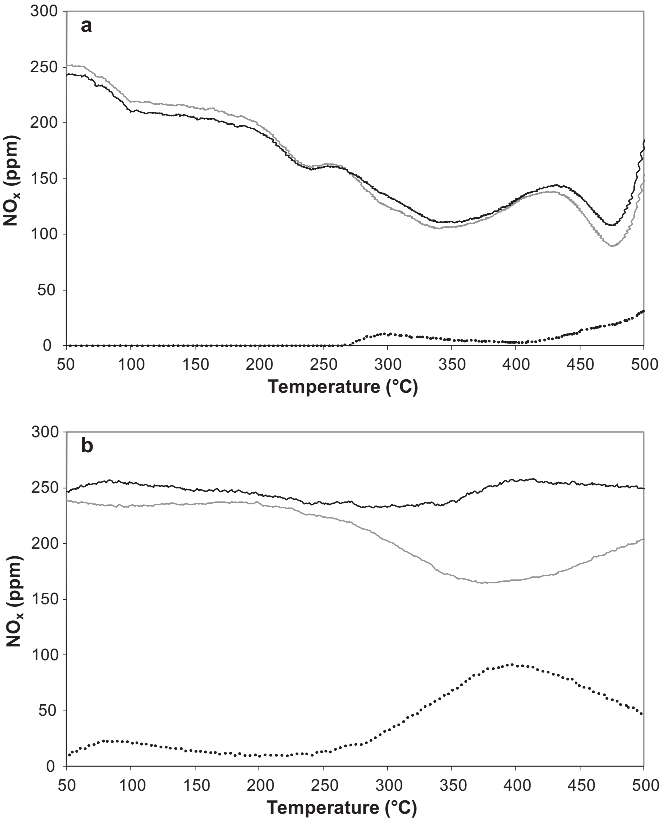

Fig. 4. TPSR profiles of NO (—), NO_2 (. . . . . .) and NO_x (**—**) with 250 ppm NO and 7 vol.% O_2 over plasma (a) and calcined (b) Co-FER catalysts; total flow of 250 mL min^{-1}.

3.2. TPSR and isothermal NO oxidation tests

Fig. 4 compares the NO oxidation TPSR profiles of plasma (a) and calcined (b) catalysts. It can be seen that the calcined catalyst exhibits two NO_2 formation peaks: a smaller peak with a maximum of 25 ppm at about 85 °C and a larger peak with a maximum of 90 ppm at about 400 °C. NO_x concentration remains constant at 250 ppm, the NO_x concentration feed into the reactor. N_2O, N_2, CO and CO_2 formation was not detected on the studied temperature range.

The plasma catalyst, on the other hand, shows almost no NO_2 formation (Fig. 4a) but presents a decrease in NO_x concentration from 65 to 480 °C. N_2O formation is detected over the plasma catalyst from 250 to 480 °C (Fig. 5). N_2 formation (m/z = 28) was also detected with two maxima at about 230 and 440 °C (Fig. 5). Regarding CO_x, although there is no CO formation over the plasma-treated sample, a low CO_2 formation occurs above 200 °C (Fig. 5).

These observations, where some NO_x reduction occurs, with the plasma-treated sample, suggest that some precursor species, arising from the catalyst preparation, still remain on the catalyst surface even after the plasma treatment, acting as reducing agent. NO reacts with these precursors to form N_2 and N_2O, which causes

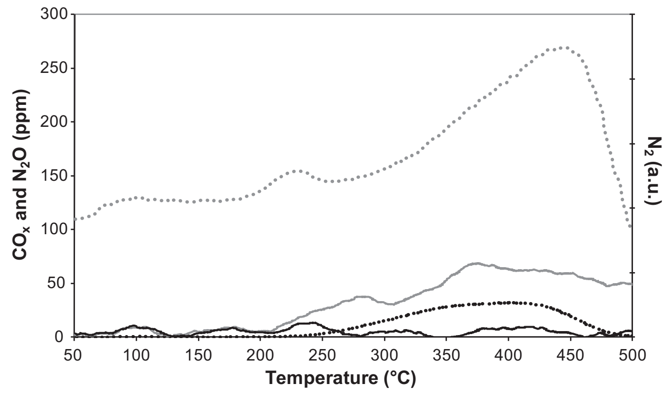

Fig. 5. TPSR profiles of CO (—), CO_2 (—), N_2O (……) and N_2 (……) with 250 ppm NO and 7 vol.% O_2 over plasma Co-FER catalyst; total flow of 250 mL min^{-1}.

a decrease in NO_x through the entire test. Taking into account the low CO_2 formation seen above 200 °C that occurs over the plasma-treated sample, which comes from *de*NO_x reaction, it is clear that not only ammonium species, identified in Section 3.1, still remain on the catalyst surface. A possible explanation for this CO_2 formation is that the acetate precursor also remained over the catalyst after the ion-exchange procedure, acting also as a reducing agent.

Therefore, it is clear that, during NO oxidation TPSR runs, plasma and calcined catalysts do not present the same ability to oxidize NO to NO_2. However, during isothermal NO oxidation tests performed with the same samples, NO_2 formation is similar in both catalysts for all the tested temperatures. This fact points out a change in the plasma catalyst during TPSR that makes its NO oxidation ability similar to the on presented by the calcined catalyst.

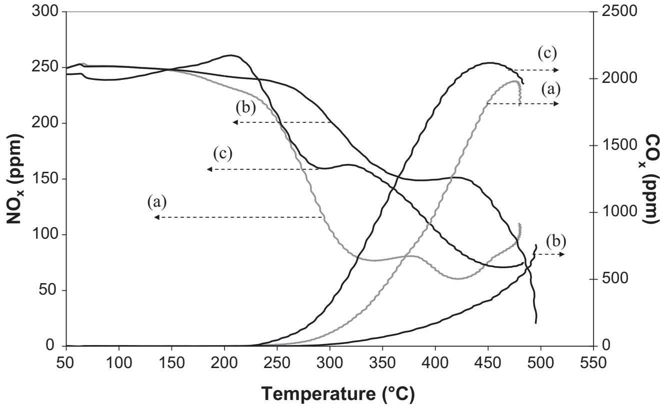

Fig. 6. TPSR profiles of NO_x and CO_x with 250 ppm NO, 1100 ppm EtOH and 7 vol.% O_2 over untreated (a), plasma (b) and calcined (c) Co-FER catalysts; total flow of 250 mL min^{-1}.

3.3. TPSR and isothermal *de*NO_x tests

The TPSR runs of untreated, plasma and calcined catalysts (Fig. 6) show that all catalysts are able to convert NO_x while presenting distinct NO_x and CO_x profiles. Plasma and calcined catalysts start NO_x conversion at about the same temperature, 150 °C.

Unexpectedly, the untreated catalyst achieves higher NO_x conversion than the calcined catalyst between 260 and 450 °C. A possible explanation for this higher catalytic activity is, as for NO oxidation TPSRs, the interaction between NO and precursors are still present on the surface of the untreated catalyst, which enhances the *de*NO_x activity. The plasma-treated sample, on the other hand, starts its NO_x conversion at a higher temperature, 260 °C.

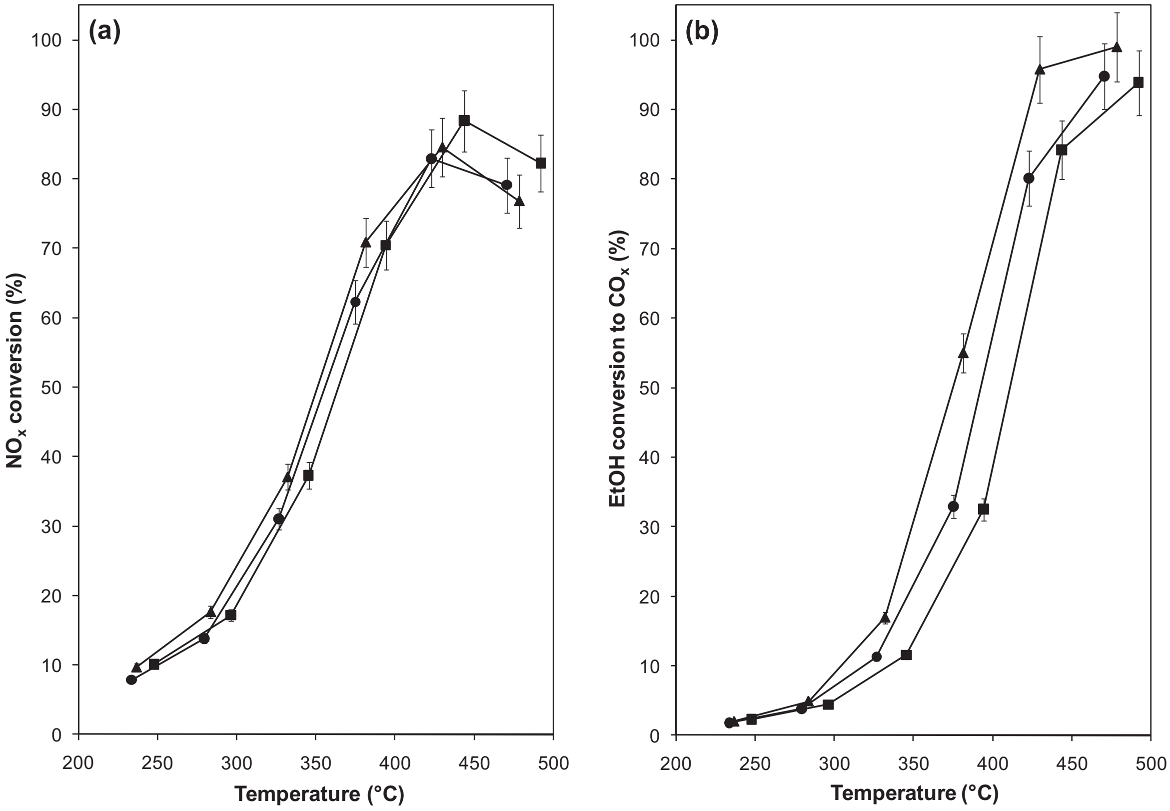

Fig. 7. Isothermal NO_x conversion (a) and ethanol conversion to CO_x (b) with 250 ppm NO, 1100 ppm EtOH and 7 vol.% O_2 over untreated (–●–), plasma (–■–) and calcined (–▲–) Co-FER catalysts; total flow of 250 mL min^{-1}.

As for CO_x formation, untreated and calcined catalysts attain both a high CO_x formation (2000 and 2100 ppm, respectively), while the plasma-treated catalyst has a maximum CO_x formation of 750 ppm at 500 °C.

Concerning the isothermal steady-state tests (Fig. 7), it can be seen that all catalysts present the same NO_x conversion and CO_x formation on the studied temperature range. Even the untreated catalyst manages to achieve the same conversion levels of calcined catalyst. NO_x conversion starts at 230 °C up to a maximum of about 85% at 430 °C (Fig. 7a), while the ethanol oxidation into CO_x increases steadily on the studied temperature range up to a maximum of 100% at 500 °C (Fig. 7b).

Comparing results obtained for the three catalysts tested under isothermal conditions (Fig. 7) with TPSR profiles (Fig. 6), several differences can be observed. Maximum NO_x conversion of each catalyst during the TPSR run is attained at different temperatures from their maximum isothermal NO_x conversions, with the exception of the untreated sample. Regarding CO_x formation, during TPSR (Fig. 6) and isothermal (Fig. 7b) tests it is similar for untreated and calcined catalysts, but not for the plasma-treated catalyst: CO_x formation during TPSR is significantly lower compared with the isothermal test.

Taking into account the striking differences between all the catalysts during the TPSR runs, it is clear that during the TPSR runs there is a modification of the surface of untreated and plasma catalysts, which results in a similar catalytic behaviour to calcined catalyst in the isothermal steps.

4. Conclusions

A combination of UV–Vis spectroscopy and TG analysis revealed the presence of ammonium ions on the untreated and plasma Co-FER catalysts but not on the calcined one. Therefore, it can be concluded that the plasma treatment was not able to replace the thermal calcination step.

NO oxidation tests showed that, during TPSR runs, calcined catalyst produces more NO_2 than plasma catalyst. NO_x conversion into N_2O and N_2 observed for plasma catalyst indicates that precursors (ammonia and acetate) used on the ion-exchange procedure are still present on the catalyst even after the plasma treatment. However, under steady-state conditions, at several temperatures, these two catalysts evidenced similar NO oxidation abilities.

Concerning *de*NOx tests using ethanol as reducing agent, TPSR tests showed higher NO_x conversions over untreated and plasma catalysts due to the presence of ammonium and acetate precursors on these catalysts. Untreated, plasma and calcined catalysts present the same NO_x and CO_x conversions in isothermal tests.

As such, the plasma treatment evaluated in this paper is not equivalent to a calcination procedure and it still needs to be optimized in order to be able to be a viable replacer for the more energetic classic treatment. One possible route could be to employ more severe plasma generating conditions in order to obtain a more energetic plasma.

Acknowledgements

The authors wish to thank to Fundação para a Ciência e Tecnologia (FCT) for financial support (grant number SFRH/BD/44108/2008).

References

[1] D. Kaucký, A. Vondrová, J. Dedecek, B. Wichterlová, Journal of Catalysis 194 (2000) 318.

[2] C.-j. Liu, G.P. Vissokov, B.W.L. Jang, Catalysis Today 72 (2002) 173.

[3] A. Brockhaus, D. Korzec, F. Werner, Y. Yuan, J. Engemann, Surface and Coatings Technology 74–75 (1995) 431.

[4] W. Xia, O.F.K. Schlüter, C. Liang, M.W.E. van den Berg, M. Guraya, M. Muhler, Catalysis Today 102–103 (2005) 34.

[5] M. Karches, M. Morstein, P. Rudolf von Rohr, R.L. Pozzo, J.L. Giombi, M.A. Baltanás, Catalysis Today 72 (2002) 267.

[6] M. Karches, C. Bayer, P. Rudolf von Rohr, Surface and Coatings Technology 116–119 (1999) 879.

[7] R. Naumann d'Alnoncourt, M. Becker, J. Sekulic, R.A. Fischer, M. Muhler, Surface and Coatings Technology 201 (2007) 9035.

[8] X. Mu, U. Bartmann, M. Guraya, G.W. Busser, U. Weckenmann, R. Fischer, M. Muhler, Applied Catalysis A: General 248 (2003) 85.

[9] s. Suvanto, T.A. Pakkanen, Journal of Molecular Catalysis A: Chemical 125 (1997) 91.

[10] R. Jafari, M. Tatoulian, W. Morscheidt, F. Arefi-Khonsari, Reactive and Functional Polymers 66 (2006) 1757.

[11] C.-j. Liu, K. Yu, Y.-p. Zhang, X. Zhu, F. He, B. Eliasson, Applied Catalysis B: Environmental 47 (2004) 95.

[12] Y. Zhao, Y.-x. Pan, L. Cui, C.-j. Liu, Diamond and Related Materials 16 (2007) 229.

[13] J.P. Breen, R. Burch, H.M. Coleman, Applied Catalysis B: Environmental 39 (2002) 65.

[14] A.A. Verberckmoes, B.M. Weckhuysen, R.A. Schoonheydt, Microporous and Mesoporous Materials 22 (1998) 165.

[15] Y. Sendoda, Y. Ono, T. Keii, Journal of Catalysis 39 (1975) 357.

[16] J. Yan, M.C. Kung, W.M.H. Sachtler, H.H. Kung, Journal of Catalysis 172 (1997) 178.

[17] D. Kaucký, J. Dedecek, B. Wichterlová, Microporous and Mesoporous Materials 31 (1999) 75.