Available online at www.sciencedirect.com
SCIENCE DIRECT®
Catalysis Today 112 (2006) 94–98
CATALYSIS TODAY
www.elsevier.com/locate/cattod

Insights into the dynamics of oxygen storage/release phenomena in model ceria–zirconia catalysts as inferred from transient studies using H_2, CO and soot as reductants

Eleonora Aneggi, Marta Boaro, Carla de Leitenburg,
Giuliano Dolcetti, Alessandro Trovarelli *

Dipartimento di Scienze e Tecnologie Chimiche, Università di Udine, via Cotonificio 108, 33100 Udine, Italy

Abstract

Samples of ceria–zirconia pre-treated under various conditions have been used as catalysts in CO and soot oxidation under stationary and transient conditions, in the presence and in the absence of oxygen. Their behaviour has been compared with that observed under redox conditions in the presence of hydrogen (oxygen storage activity). All the catalysts are active in CO and soot oxidation. Under stationary conditions, the activity in CO oxidation depends on the amount of Ce present, with little contribution from the redox capacity of the support and is strongly influenced by surface area. When the reaction is carried out under transient conditions, especially with low-surface area samples, the performances of ceria–zirconia are higher than those of ceria, with a maximum in the middle composition range. Interestingly, a similar behaviour is observed in soot combustion, where the activity for low-surface area sample is dependent on composition. This suggests that oxygen from the support plays a key role also in the oxidation of large carbon particles under a fully oxidizing mixture.

Keywords: Ceria; Ceria–zirconia; CeO_2; Soot oxidation; CO oxidation; Oxygen storage capacity

1. Introduction

The mechanism controlling the reduction and oxidation features of ceria and ceria–zirconia is a key issue in the development of efficient catalyst formulations for three-way catalysts. Several investigations have been carried out trying to understand the most important factors affecting the reduction of Ce^{4+} in ceria or ceria–zirconia under various experimental conditions, with a focus on the effect of composition, structural, textural and morphological features on the oxygen storage phenomena [1]. However, there are still some points that need further investigation, especially those associated to the dynamic behaviour of the catalysts and to the effect of different environments. Recently, the effects of noble metals in the dynamic behaviour of CO oxidation over ceria and ceria–zirconia have been addressed focusing mainly on structural [2] and kinetic/mechanistic issues [3–6]. CO oxidation under dynamic conditions in the absence of noble metals has also been previously addresses with a special focus on the role of bulk and surface phenomena [7–9]. In order to gain further insights into the dynamic of oxygen storage with its implication in catalysis, (and to study the role of the nature of the reducing agent), we investigate here the behaviour of ceria-zirconia ($Ce_xZr_{1-x}O_2$, $0 \leq x \leq 1$) as catalyst in soot combustion and in CO oxidation under cycling and steady state conditions. A comparison of the behaviour of the catalysts under hydrogen is also carried out. The main objective of the study is to understand (i) if, and to what extent, oxygen storage is a key factor in affecting the activity of the catalysts under apparently different environments; (ii) how does bulk and surface properties (especially those related to oxygen mobility) affect catalytic behaviour in all these reaction environments, and (iii) which are the typical characteristics of the catalytic behaviour when redox phenomena are governing activity in all the composition range investigated.

---

* Corresponding author. Tel.: +39 0432 558 855; fax: +39 0432 558 803.
E-mail address: trovarelli@uniud.it (A. Trovarelli).

0920-5861/$ – see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.cattod.2005.11.019

2. Experimental

The catalysts (with formal composition $Ce_xZr_{1-x}O_2$, with $0 \leq x \leq 1$) were commercial samples prepared by coprecipitation (Grace Davison Inc.). Their characteristics are reported in Table 1. For brevity samples are indicated as CZXX where XX is the molar amount of CeO_2 in mixed oxides. Materials subjected to three different pre-treatment were employed in the catalytic studies: fresh samples (FCZXX) were calcined at low temperature (773 K); aged samples (ACZXX) were obtained from fresh catalysts after treatment under air at 1023 K for 12 h; redox aged materials (RCZXX) were obtained by heating the fresh sample under H_2(5%)/N_2 mixture up to 1273 K and then cooling down to 823 K for reoxidation. Similar procedures are known to activate catalysts toward oxygen release [10–12].

Structural features of the catalysts were characterized by powder X-ray diffraction. Oxygen storage capacity under hydrogen atmosphere was measured using a thermal gravimetric analysis (TGA, Q-500). The weight loss of samples was measured against time when flowing a mixture of 5% H_2 in nitrogen at 673 K for 30 min over an open crucible containing ca. 20 mg of sample. The samples for soot oxidation activity were prepared by accurately mixing the catalyst with soot (Printex-U, Degussa) in a mortar for 10 min in order to achieve a tight contact [13]. A catalyst:soot weight ratio of 20:1 was adopted. Catalytic tests were carried out by running TPO experiments in a thermo gravimetric apparatus heating at 10 K/min from 423 to 1073 K under an air flow (60 ml/min). Reproducibility of experiments in terms of T50 was within 4 K. Soot oxidation under anaerobic conditions was carried out by using the same procedure with nitrogen instead of air and using a catalyst:soot ratio of 115:1. CO oxidation reaction was carried out under stationary and cycled feedstream conditions as recently reported [7,8]. Cycling operation was obtained using a system of electronically driven valves switching at a desired frequency. The reactor consisted of a 6 mm-od. by 4 mm-id. by 300 mm-long quartz tube. The powdered catalyst (0.06–0.08 g) was loaded after being mixed with an equal amount of quartz beads. A total flow of 90 ml/min was used with a GHSV = 108,000 h^{-1}. The composition was cycled alternately between CO(4%), He and O_2(2%), with cycling consisting of 5 s in CO, 5 s in He, 5 s in O_2 and 5 s in He with 20 s being the time period between two CO or O_2 consecutive pulses. Measurements under stationary conditions were carried out in the same reactor, with a total flow of 100 ml/min. Activity was measured by running a temperature programmed experiment from room temperature to 1273 K and measuring conversion using an on-line infrared analyzer and paramagnetic O_2 analyzer (ABB). Typical feed conditions were CO(2%), O_2(1%), N_2 as diluent.

3. Results and discussion

3.1. Textural and structural characterization

Textural and structural characterization of samples are reported in Table 1. The effect of aging in all samples results in a drop of surface area, more pronounced with Zr-free materials, in agreement with previous findings [14,15]. XRD measurements suggest that for sample with cerium content greater than 75 mol% the formation of a cubic fluorite lattice is favoured. This is in accordance with literature, where generally the limit for formation of a cubic (either cubic or t'') solid solution is found at ca. 50 mol% CeO_2 [16]. In the range of composition 25–45 mol% CeO_2 good agreement between the refinement and a tetragonal structural model confirms that all samples belong to the t' tetragonal phase with space group $P4_2/nmc$. No peak splitting that would indicate the presence of two phases could be detected, and therefore, the diffraction patterns demonstrate the formation of a single solid solution like ceria–zirconia phase. However, this cannot exclude the presence of different arrangements of oxygen sublattice or the presence of a multiphase system at a nanoscale level, not detected by XRD [17].

Table 1
Structural and textural characteristics of samples used in this study

Sample	Phase	Cell parameters[a]			B.E.T. (m^2/g)	Particle size (nm)[b]
		$a = b = c$ (Å)	$a' = b'$ (Å)	c (Å)		
FCZ100	Cubic	5.411			57	11.2
ACZ100	Cubic	5.410			22	35.6
RCZ100	Cubic	5.411			7	>70
FCZ75	Cubic	5.370			73	6.3
ACZ75	Cubic	5.370			44	10.1
RCZ75	Cubic	5.351			10	20.9
FCZ44	Tetragonal t'		5.251	5.346	96	4.7
ACZ44	Tetragonal t'		5.250	5.341	54	6.9
RCZ44	Tetragonal t'		5.261	5.293	13	15.6
FCZ28	Tetragonal t'		5.177	5.261	100	6.2
ACZ28	Tetragonal t'		5.175	5.266	58	8.5
RCZ28	Tetragonal t'		5.203	5.251	13	12.5
FCZ0	Tetr. 25%[c] mon. 75%	Not refined	Not refined	Not refined	79	11.8
ACZ0	Tetr. 17%[c] mon. 83%	Not refined	Not refined	Not refined	44	15.9
RCZ0	Tetr. 8%[c] mon. 92%	Not refined	Not refined	Not refined	10	23.4

[a] Calculated from Rietveld refinement.

[b] Calculated with Scherrer formula from X-ray diffraction patterns.

[c] Value calculated from RIR method.

3.2. Behaviour under hydrogen atmosphere

Samples described in Table 1 have been subjected to TGA cycles under hydrogen atmosphere. From the shape of the TG profiles (by considering the initial slope of the weight-loss versus time curve) it is possible to calculate values of initial oxygen removal rates. Total oxygen storage can also be calculated from the ultimate weight-loss values after 30 min on stream; the data are reported in Fig. 1. O_2 removal rate curves calculated on a per gram basis (Fig. 1A) show a maximum that fluctuates with composition, depending on pre-treatment, with fresh samples being the most active. If we separate the surface contribution, by computing the rate of oxygen extracted per unit surface area, the initial rate increases with the amount of cerium showing a maximum with ceria. However, for pure ceria the rate rapidly decreases to negligible values after a few minutes; in contrast for CZ(<100) compositions the rate remains at high values for several minutes on stream. By comparing the oxygen extracted at the beginning of reaction to the theoretical OSC values calculated per unit surface area [9], it can be concluded that only with redox-aged samples of composition CZ75, CZ44 and CZ28 bulk oxygen atoms participate to the reaction.

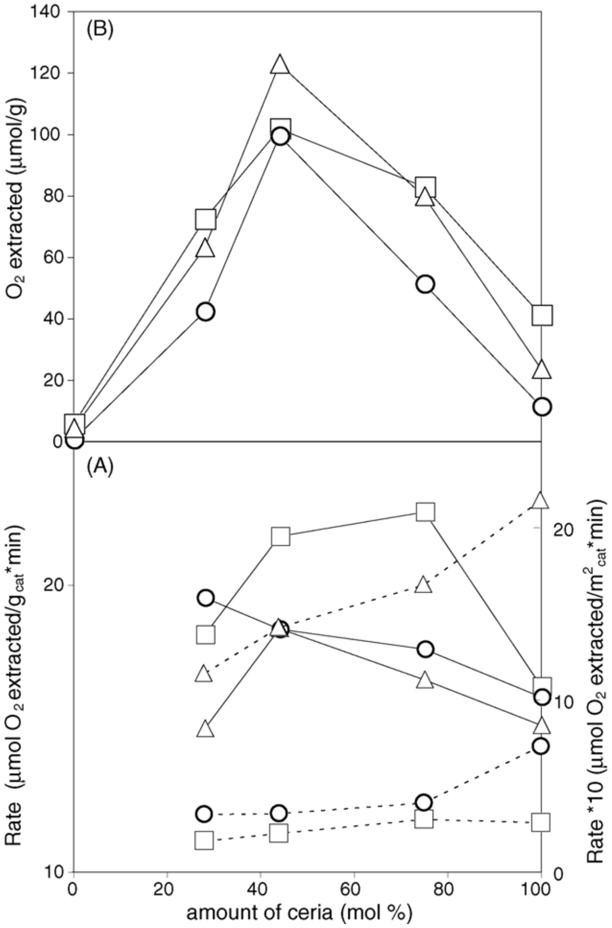

Fig. 1. A: Initial oxygen removal rate on a per gram (— left) and surface basis (··· right) at 673 K under H_2(5%)/N_2; □ fresh samples, ○ aged samples, △ redox-aged samples; B: total oxygen removed after 30 min of reaction at 673 K under H_2(5%)/N_2.

A more defined behaviour with a maximum at the composition CZ44 is observed in total oxygen storage for the three series of samples (Fig. 1B). It seems that aging causes a drop of oxygen storage activity which is much more evident in ceria and zirconia-rich compositions; redox ageing is beneficial for CZ44, with an increase of ca. 20% in oxygen extracted on RCZ44 compared to FCZ44, while O_2 removal is similar in fresh and redox-aged samples of the other compositions. The above picture is consistent with modification of oxygen sublattice upon redox-aging in RCZ44 compared to FCZ44, which increase the mobility of oxygen ions, thus enhancing total O_2 extracted [17]. The finding of a maximum [10,18–20] can be explained assuming that the intermediate composition meets the requirements of two opposite tendencies. From one side the increase of number of active redox elements (i.e. cerium ions) should bring to an increase in the total O_2 available upon reduction; from the other side, upon diluting ceria with zirconia, the structural features of the mixed oxide lattice are modified by stabilizing tetragonal t' and t'' phases, which are more reactive toward oxygen extraction from the bulk. This benefit could be the result of the high oxygen transport properties typical of the fluorite lattice, coupled with the presence of structural defects (like oxygen distortions) which enhance diffusion of oxygen [21,22]. The fact that the maximum in dynamic experiments is not at a fixed composition indicates a strong sensitivity of O_2 extraction rate to local surface and sub-surface arrangements; in general, ceria and ceria-rich materials have a higher surface reactivity with a lower rate of oxygen extraction from the bulk compared to other compositions. In additions, rate values are certainly dependent on composition and treatments and may considerably vary between series of homologous samples.

3.3. CO oxidation under stationary and cycling conditions

The light-off curve has been used to study the performance of catalyst in CO oxidation under stationary conditions. Determination of activity has been carried out by measuring the rate of CO oxidation at low conversions (from the conversion versus temperature curves) assuming differential reactor conditions, under a kinetically controlled regime. Fig. 2 displays the results obtained; for better clarity, rate values have been normalized to those obtained with pure ceria. Specific activity under stationary conditions shows a marked dependence on the amount of cerium present, regardless of thermal pre-treatment. Under cycling conditions, a plot showing a maximum of activity in the middle composition range is observed with an increase of activity for middle range composition after redox ageing. It seems therefore that cerium is responsible for the activity of the mixed oxides under stationary conditions while the presence of zirconium significantly contributes to the activity changes observed in oscillating mode. In the first case the activity is almost proportional to exposed cerium site, in contrast, an optimum composition with a maximum in reaction rate characterizes activity under cycling mode where oxygen from the bulk is involved in every CO oxidation cycle. The increase of activity

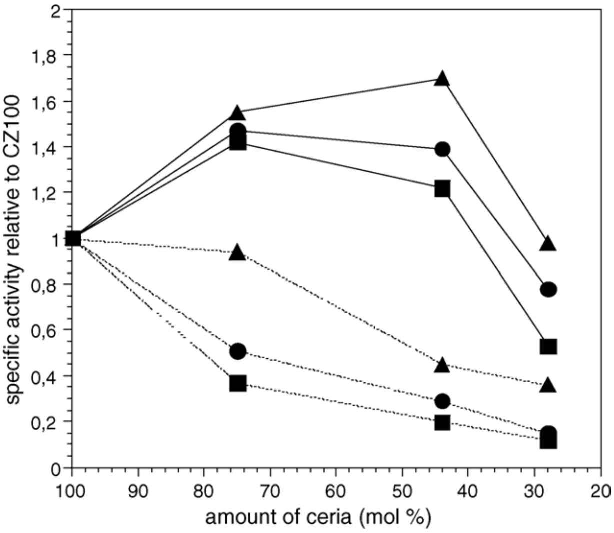

Fig. 2. Comparison of the rate of CO oxidation at 553 (calculated per unit surface area) obtained under stationary conditions (dotted lines) and cycling conditions (solid lines): ■ fresh samples, ● aged samples, ▲ redox-aged samples. For clarity turnover data have been refereed to pure ceria.

in the middle composition range is higher for low surface area samples (especially redox-aged) indicating that for this composition a higher contribution of oxygen extraction from the bulk to the overall activity is observed, in agreement with results obtained using H_2 as reductant.

3.4. Soot oxidation under stationary and anaerobic conditions

Among the several techniques that have been developed for reducing emissions from diesel engines, filtering followed by catalytic oxidation is one of the more promising. In the catalytic approach the system is based on the use of a catalyst to achieve the onset of regeneration at a significantly lower temperature [13]. Regarding the intimate mechanism involved in oxidation of carbon, several authors pointed out the importance of redox properties of the catalyst, and the use of supports based on cerium oxide is shown to confer interesting properties to soot combustion catalysts [22–26]. We have therefore compared the properties of ceria and ceria–zirconia in the combustion of soot.

All the catalysts examined are active in promoting soot combustion in the range of temperature from ca. 600 to 800 K. As a measure of activity we used the temperature at which 50% of weight loss is observed (T50%, corresponding to removal of 50% of soot), Fig. 3A. Although these data do not have a true kinetic meaning, they can be used for a qualitative comparison with T50 obtained in CO oxidation under stationary conditions. For FCZ samples the order of reactivity is dependent on Ce content, with the lowest T50 value obtained with cerium-rich compositions. After ageing there is an increase of the oxidation temperature which is higher with CZ100 and CZ0; as a consequence the curve assumes a volcano-type profile with a minimum in the middle composition range, characteristic of phenomena driven by the redox features of the catalyst. The role of oxygen storage can be well evidenced by conducting a series of TG experiments in the absence of air, under inert gas flow; a sort of temperature programmed reduction under nitrogen and using soot as reductant. The TG profiles (not reported for brevity) show a continuous weight loss starting at ca. 500 K with evolution of oxygen and CO_2. The results are reported in Fig. 3B. The behaviour closely resembles that observed under H_2 or under CO oxidation under cycling mode, thus pointing out that participation of lattice oxygen in soot oxidation may contribute to overall activity, especially when surface area is low (and in the presence of redox-activated samples) or in the presence of large soot particles, when access of gas phase oxygen is limited also by geometrical factors. This is also the reason for using ceria as promoter in the combustion of bulky VOC emitted from restaurants [27].

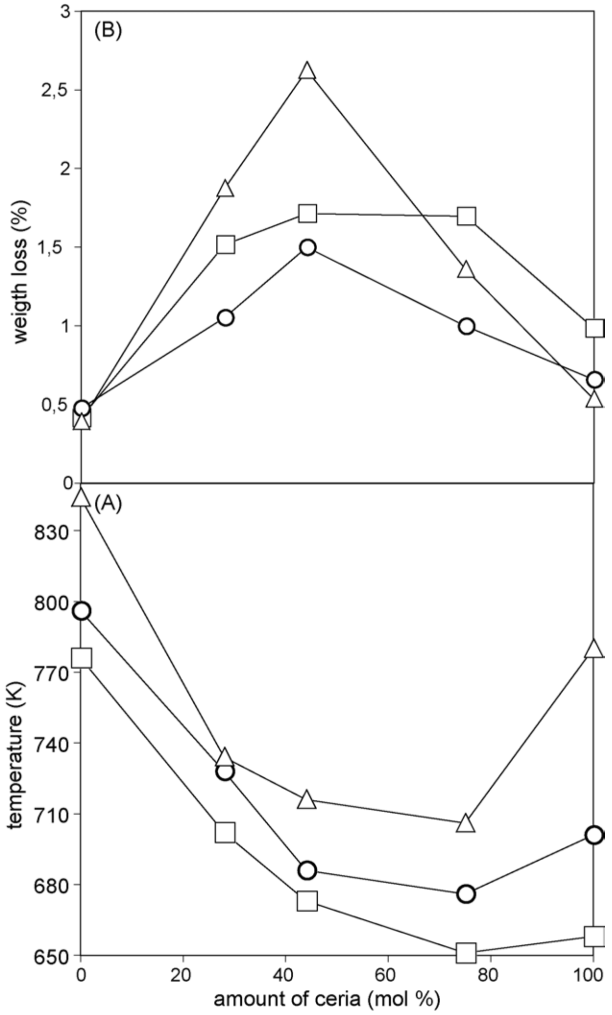

Fig. 3. A: T50 against composition as obtained from TG experiment on soot/catalyst mixtures under air; □ fresh samples, ○ aged samples, △ redox-aged samples. B: weight-loss against catalyst composition of soot/catalysts samples subjected to temperature gradient under anaerobic conditions after blank substraction.

Due to the similarity in the behaviour of CO and soot oxidation an hypothesis of mechanism can be put forward, in analogy to what has been done for CO oxidation, by invoking a redox mechanism with a simple redox route for soot oxidation, which utilizes oxygen activated from the support in a typical reduction/oxidation mechanism (Mars–Van–Krevelen type) in which the catalyst undergoes a partial reduction. Oxygen storage is therefore important because it provides an alternative route for the oxidation of big soot particles. An alternative redox route involves oxygen from the support and gas-phase which reacts with soot to form adsorbed CO_2 in the form of carbonates. Decomposition of carbonate is then stimulated by gas phase oxygen that provides also reoxidation of the support.

3.5. Summary and conclusions

In summary, the results presented here show evidence that hydrogen, CO and soot particles can be effectively used to monitor the redox activity of ceria–zirconia. When reactions are carried out under anaerobic conditions a typical volcano-type plot characterizes activity behaviour against composition, with a maximum in the middle composition range and a minimum with ZrO_2. The effect being more pronounced with low surface area materials where the behaviour is closely correlated with that found with hydrogen. In the presence of oxygen, although the mechanism still rely upon reduction and oxidation of the support, the continuous supply of gas-phase oxygen make the reaction rate dependent on available surface sites and therefore reactivity becomes a function of surface Ce ions. By lowering surface area the participation of oxygen from lattice, especially in ceria–zirconia is more likely to occur, although this still represents a minority in the overall contribution to reaction rate.

Acknowledgments

The authors thank financial support from MIUR (progetti PRIN). We are also grateful to Grace Davison for providing samples used in this study.

References

[1] R. Di Monte, J. Kaspar, Top. Catal. 28 (2004) 47.

[2] A. Martorana, G. Deganello, A. Longo, A. Prestianni, L. Lotta, A. Macaluso, G. Pantaleo, A. Balerna, S. Mobilio, J. Solid State Chem. 177 (2004) 1268.

[3] R. Rajasree, J.H.B.J. Hoebink, J.C. Schouten, J. Catal. 223 (2004) 36.

[4] S.Y. Christou, C.N. Costa, A.M. Efstathiou, Top. Catal. 30/31 (2004) 325.

[5] P.S. Lambrou, C.N. Costa, S.Y. Christou, A.M. Efstathiou, Appl. Catal. B: Env. 54 (2004) 237.

[6] F. Dong, A. Suda, T. Tanabe, Y. Nagai, H. Sobukawa, H. Shinjoh, M. Sugiura, C. Descorme, D. Duprez, Catal. Today 93–95 (2004) 827.

[7] M. Boaro, C. de Leitenburg, G. Dolcetti, A. Trovarelli, J. Catal. 193 (2000) 338.

[8] M. Boaro, F. Giordano, S. Recchia, V. Dal Santo, M. Giona, A. Trovarelli, Appl. Catal. B: Environ. 52 (2004) 225.

[9] Y. Madier, C. Descorme, A.M. LeGovic, D. Duprez, J. Phys. Chem. B 103 (1999) 10999.

[10] H. Vidal, J. Kaspar, M. Pijolat, G. Colon, S. Bernal, A. Cordon, V. Perrichon, F. Fally, Appl. Catal. B: Environ. 27 (2000) 49.

[11] L.F. Liotta, A. Macaluso, A. Longo, G. Pantaleo, A. Martorana, G. Deganello, Appl. Catal. A: Gen. 240 (2003) 295.

[12] S. Bernal, G. Blanco, M.A. Cauqui, P. Corchado, J.M. Pintado, J.M. Rodriguez-Izquierdo, Chem. Commun. (1997) 1545.

[13] B.A.A.L. van Setten, M. Makkee, J.A. Moulijn, Catal. Rev. Sci. Eng. 43 (2001) 489.

[14] V. Perrichon, A. Laachir, S. Abournadasse, O. Touret, G. Blanchard, Appl. Catal. A: Gen. 129 (1995) 69.

[15] J. Kaspar, P. Fornasiero, in: A. Trovarelli (Ed.), Catalysis by Ceria and Related Materials, Imperial College Press, London, 2002 , pp. 217–241.

[16] J. Kaspar, P. Fornasiero, M. Graziani, Catal. Today 50 (1999) 285.

[17] E. Mamontov, R. Brezny, M. Koranne, T. Egami, J. Phys. Chem. B 107 (2003) 13007.

[18] A. Trovarelli, F. Zamar, J. Llorca, C. de Leitenburg, G. Dolcetti, J. Kiss, J. Catal. 169 (1997) 490.

[19] H. Vidal, J. Kaspar, M. Pijolat, G. Colon, S. Bernal, A. Cordon, V. Perrichon, F. Fally, Appl. Catal. B: Environ. 30 (2001) 75.

[20] S. Rossignol, F. Gérard, D. Duprez, J. Mater. Chem. 9 (1999) 1615.

[21] A. Trovarelli, M. Boaro, E. Rocchini, C. de Leitenburg, G. Dolcetti, J. Alloy. Compd. 323/324 (2001) 584.

[22] M.L. Pisarello, V. Milt, M.A. Peralta, C.A. Querini, E.E. Miro’, Catal. Today 75 (2002) 465.

[23] E.E. Miro’, F. Ravelli, M.A. Ulla, L.M. Cornaglia, C.A. Querini, Catal. Today 53 (1999) 631.

[24] G. Neri, G. Rizzo, S. Galvagno, M.G. Musolino, A. Donato, R. Pietropaolo, Thermochim. Acta 381 (2002) 165.

[25] J.F. Lamonier, N. Sergent, J. Matta, A. Aboukaïs, J. Therm. Anal. Calorimetry 66 (2001) 645.

[26] A. Setiabudi, J. Chen, G. Mul, M. Makkee, J.A. Moulijn, Appl. Catal. B 51 (2004) 9.

[27] J.C. Fu, L. Czarnecki, C. Patellis, A. Bouney, W.A. Whittenberger, in: Proceedings of the Air Waste Management Association, 92nd Annual Meeting, St. Louis, MI, 1999), pp. 99–217.