Promotional effect of C$_2$–C$_4$ hydrocarbon on CH$_4$ oxidation on sulfated Pt/γ-Al$_2$O$_3$ catalysts

Griselda Corro [a,*], Carlos Cano [a], J.L.Garcia Fierro [b]

[a] *Instituto de Ciencias, Benemérita Universidad Autónoma de Puebla,
14 Sur 6301, Puebla, Puebla 72570, Mexico*
[b] *Instituto de Catálisis y Petroleoquímica, CSIC, Cantoblanco, 28049 Madrid, Spain*

Available online 13 November 2007

Abstract

The addition of the alkanes C$_2$H$_6$, C$_3$H$_8$, or n-C$_4$H$_{10}$ in the CH$_4$–O$_2$–SO$_2$ reaction feed resulted in an improvement of pre-sulfated 1% Pt/γ-Al$_2$O$_3$ activity on CH$_4$ oxidation in lean conditions. These results are explained assuming that (i) the energy generated during the oxidation of the alkanes may be transferred to activate the rate determining step of CH$_4$ oxidation, over the catalyst surface, increasing the reaction rate at lower temperatures and (ii) alkanes oxidation may lower the coverage of oxygen on the Pt surface, leaving surface active sites free for CH$_4$ adsorption, thus increasing its oxidation rate, since, oxygen species act as an inhibitor for the reaction at full coverage. n-C$_4$H$_{10}$ addition in the reaction feed generated the highest promotion on CH$_4$ complete oxidation. This promotional effect was further increased on pre-sulfated 2% Pt/γ-Al$_2$O$_3$. Results presented in this investigation suggest that small amounts of n-butane in the gas feed during CH$_4$–O$_2$ reaction over a pre-sulfated Pt/γ-Al$_2$O$_3$ catalyst may eliminate completely very low concentrations of methane emissions at low temperatures from lean-burn NGV exhausts.
© 2007 Published by Elsevier B.V.

Keywords: Methane oxidation; NGVs emissions; Sulfated Pt catalysts; Sulfur deactivation resistance

1. Introduction

Natural gas represents one promising alternative energy source for the future in automotive and heavy-duty vehicles. In comparison with traditional fuelled vehicles, lean-burn natural gas vehicles (NGV) generate a lower impact on environment, due to smokeless exhausts and reduced nitrogen oxide emissions due to the lower combustion temperatures associated with the high air to fuel mass ratios (20 or greater) at which the lean engine operates. Also tailpipe CO$_2$ emissions in NGV light-duty vehicles can be lower than in conventional fuelled vehicles due to the higher hydrogen-to-carbon ratio of natural gas. Natural gas engines can operate under lean conditions so that the fuel efficiency can be increased compared to stoichiometric conditions. Under these conditions, unburned methane, a potent greenhouse gas, is emitted in the exhaust gases. Accordingly, severe limitations on CH$_4$ emissions have been enforced [1]. In order to meet these severe regulations, a catalytic exhaust converter has to be installed on lean-burn heavy-duty NGVs. This device is designed to achieve methane emission abatement by catalytic combustion. However, difficulties arise due to the high stability of the CH$_4$ molecule and from the reaction conditions specific to lean-burn engines. Typical exhaust gases are characterized by low temperatures (less than 500–550 °C), low concentrations of CH$_4$, large amounts of water vapor, large excess of oxygen and presence of SO$_2$ and NO$_x$.

The complete oxidation of methane can be performed over either noble metals or transition metal oxides [2–5]. Pd/γ-Al$_2$O$_3$ catalysts are widely recognized as the most active in combustion of methane [1,6–14], but are deactivated by water and sulfur containing compounds present in the exhaust. Platinum catalysts properties in the complete oxidation of methane at low temperature have been less studied. It has been shown that Pt has a very poor activity for methane oxidation, but would be more resistant to sulfur poisoning [6,10]. By adding small amounts of platinum into the palladium catalyst, relative improved activity was obtained in comparison with the monometallic palladium catalyst for complete oxidation of methane [15,16].

Now, in recent investigations, we found a strong promotional effect of the presence of 1000 ppmV C$_3$H$_8$ in the reaction feed on CH$_4$–SO$_2$–O$_2$ reaction over pre-sulfated Pt/γ-Al$_2$O$_3$ [17] and pre-sulfated Pt–Sn/γ-Al$_2$O$_3$ [18] catalysts. Moreover, the

* Corresponding author.
E-mail address: cs001380@siu.buap.mx (G. Corro).

catalysts showed no deactivation due to the SO_2 present in the gas feed. These results were obtained using a reaction feed containing a concentration of 2 vol% CH_4, which is higher relative to the concentration of methane in a real NGV exhaust (as low as 1000 ppmV) [9,19]. This promotional effect of propane was explained in terms of (i) the propane combustion heat which may be transferred, to activate the abstraction, of the first hydrogen of the adsorbed methane molecule and (ii) to propane oxidation that may lower the high coverage of oxygen on the Pt surface, leaving surface active sites free for CH_4 adsorption. In order to confirm these explanations, in this study, we investigated the effect of the presence of other alkanes with different combustion heats [20] and different number of carbon atoms. Therefore, we studied the effect of the presence of ethane, propane or n-butane on the activity of pre-sulfated Pt/γ-Al_2O_3 catalysts on CH_4–O_2–SO_2 reaction using a reaction feed containing a low concentration of methane (2000 ppmV) in excess oxygen and in the presence of SO_2.

2. Experimental

The support used was γ-Al_2O_3 Merck with a grain size of 0.063–0.200 mm (70–230 mesh ASTM). Before use, the support was calcined for 6 h at 600 °C in air. Pt catalysts supported on alumina were prepared by impregnation using acidic aqueous solution (0.1 M HCl) of H_2PtCl_6·$6H_2O$ (Merck, minimum 98% purity). After impregnation, the catalysts were dried at 120 °C overnight, and then, calcined in flowing air for 6 h at 500 °C. Finally, the catalysts were reduced in pure hydrogen flow for 8 h at 500 °C. A reference alumina support was prepared in the same way using only diluted hydrochloric acid.

A sample of the reduced catalyst was then sulfated. Sulfation was performed on samples heating to 500 °C in flowing air (100 cm^3 min^{-1}). The feed was then changed at 500 °C for a nitrogen flow containing 50 ppm SO_2, 5% O_2 (100 cm^3 min^{-1}) for 10 h. The sample was then cooled to 25 °C.

Platinum accessibility measurements on the reduced catalysts were obtained by the H_2–O_2 titration method at room temperature in a static volumetric apparatus and using the stoichiometric $(H/Pt)_{surf} = 1$. The chemical microanalysis of the catalyst was determined by energy dispersive X-ray spectroscopy (EDS), (NORAN) performed in conjunction with a scanning electron microscope (JEOL, model JSM-6300). Catalysts metal contents are reported in Table 1.

Photoelectron spectra were recorded over pre-sulfated fresh sample using a VG Escalab 200R electron spectrometer equipped with a hemispherical analyzer, operating in a constant pass energy mode, and a non-monochromatic Mg Kα ($hν$ = 1253.6 eV, 1 eV = 1.603×10^{-19} J) X-ray source operated at 10 mA and 12 kV. The energy regions of the photoelectrons

of interest were scanned a number of times in order to get good signal-to-noise ratios. The intensities of the peaks were estimated by determining the integral of each peak after subtracting an S-shaped background and fitting the experimental peak to Lorentzian/Gaussian lines (80% L/20% G). The binding energies (BE) were referenced to the Al 2p peak, the BE of which was fixed at 74.5 eV. Using this reference, BE values of C 1s peak coming from adventitious carbon appeared at 284.9 ± 0.2 eV.

The catalysts tests were performed in a continuous flow tubular quartz reactor (inner diameter 7 mm) placed in a programmable furnace. The catalyst temperature was controlled by a thermocouple mounted internally in direct contact with the sample in order to read the true catalyst temperature. Measurements over the catalysts were performed using a feed volume flow rate of 100 cm^3 min^{-1} consisting of 2000 ppmV CH_4, 20 vol% of O_2, 50 ppmV SO_2, without or with C_2H_6 or C_3H_8, or n-C_4H_{10} (2000 ppmV, 1333 ppmV, 666 ppmV, or 333 ppmV) and balance N_2. The catalyst loading was of 200 mg. The reactor out flow was analyzed using a gas chromatograph (GC-17 Shimadzu) equipped with a thermal conductivity detector. Two consecutive heating and cooling cycles at temperatures from 25 to 600 °C were conducted; the results from the second cycle were used in this study. The conversions of CH_4, C_2H_6, C_3H_8, or n-C_4H_{10} to all products were calculated based on the following equation:

$$conversion\,(\%) = \frac{X_{in} - X_{out}}{X_{in}} \times 100$$

X_{in} is the concentration of X introduced in the experiment and X_{out} is the concentration of X at the reactor outlet.

3. Results

3.1. Catalysts characterization

The catalyst characterization data are summarized in Table 1. Pt dispersion values of 0.35 and 0.30 were obtained for unsulfated 1% Pt/γ-Al_2O_3 and 2% Pt/γ-Al_2O_3, respectively.

Pt dispersion values for the catalysts after reaction or after sulfation were not determined because the samples needed to be reduced again under a H_2 atmosphere at 100 °C to reduce the Pt. This reduction might have led to the reduction of sulfate to H_2S which poisons Pt sites.

3.2. Methane oxidation

Pre-sulfated γ-Al_2O_3 was not active for methane oxidation at the temperatures studied in this work, in the presence and in the absence of C_2H_6, C_3H_8, or n-C_4H_{10}.

Table 1
Catalysts characterization data

Catalyst	Pt (wt%)	Pt dispersion	Pt surface atoms ($\times 10^{-18}$ g^{-1})	Cl (wt%)	S (wt%)
Pre-sulfated 1% Pt/γ-Al_2O_3	1.02	0.35	10.80	1.1	1.65
Pre-sulfated 2% Pt/γ-Al_2O_3	2.01	0.30	18.52	1.1	1.60

Table 2
CH_4 light-off$_{50}$ values obtained for methane oxidation in CH_4–O_2–SO_2 reaction in the presence of alkanes in the feed

Catalyst (pre-sulfated)	Alkane	Alkane combustion heat $(-\Delta H_C^{\circ})$ kcal mol^{-1}	Alkane concentration (ppmV)	Light-off$_{50}$ CH_4 (°C)
1% Pt/γ-Al$_2$O$_3$	–	–	–	570
	C_2H_6	372.8	333	550
			666	550
			1333	540
			2000	534
	C_3H_8	530.6	333	546
			666	535
			1333	511
			2000	500
	n-C_4H_{10}	687.9	333	520
			666	513
			1333	480
			2000	465
2% Pt/γ-Al$_2$O$_3$	n-C_4H_{10}	687.9	2000	430

Table 2 reports the temperatures at which 50% CH_4 conversion (light-off$_{50}$) for methane oxidation in CH_4–O_2–SO_2 reaction are reached in the presence of different concentrations of the alkanes in the feed for pre-sulfated 1% Pt/γ-Al$_2$O$_3$ catalyst. The evolution of methane conversion in CH_4–O_2–SO_2 reaction over pre-sulfated 1% Pt/γ-Al$_2$O$_3$ catalyst in the presence and in the absence of 2000 ppmV C_2H_6, C_3H_8, or n-C_4H_{10} is shown in Fig. 1. In this figure and in Table 2 it can be observed that the presence of C_2H_6, C_3H_8, or n-C_4H_{10}, results in a lowering of the CH_4 light-off$_{50}$ values on pre-sulfated 1% Pt/γ-Al$_2$O$_3$ catalyst. This decrease is stronger as the alkane concentration in the feed increases and as the number of carbon atoms in the alkane molecule increases.

In Table 2, CH_4 light-off$_{50}$ values obtained for methane oxidation in CH_4–O_2–SO_2 reaction in the presence of 2000 ppmV n-C_4H_{10} are also reported for 2% Pt/γ-Al$_2$O$_3$ catalyst. A further strong enhancement on CH_4–O_2 reaction resulted from increasing Pt content in the catalyst. In Fig. 2 the evolution of CH_4 conversion in CH_4–n-C_4H_{10}–O_2–SO_2 reactions over pre-sulfated 1% Pt/γ-Al$_2$O$_3$ and pre-sulfated 2% Pt/γ-Al$_2$O$_3$ catalyst is shown. It is evident that the increase in platinum content in the catalyst resulted in an increase of the catalyst activity on methane oxidation.

3.3. X-ray photoelectron spectroscopy

Binding energies of core electrons of pre-sulfated 1% Pt/γ-Al$_2$O$_3$ and pre-sulfated 2% Pt/γ-Al$_2$O$_3$ catalyst are reported in Table 3. Two components were observed; one at the lower binding energies (315.4 eV) associated with metallic platinum. The binding energy of the Pt 4d$_{5/2}$, revealed a higher binding energy component (318.5 eV) that can be associated to a more oxidized species of Pt (Pt^{4+}) [21–24]. The binding energies of Pt species
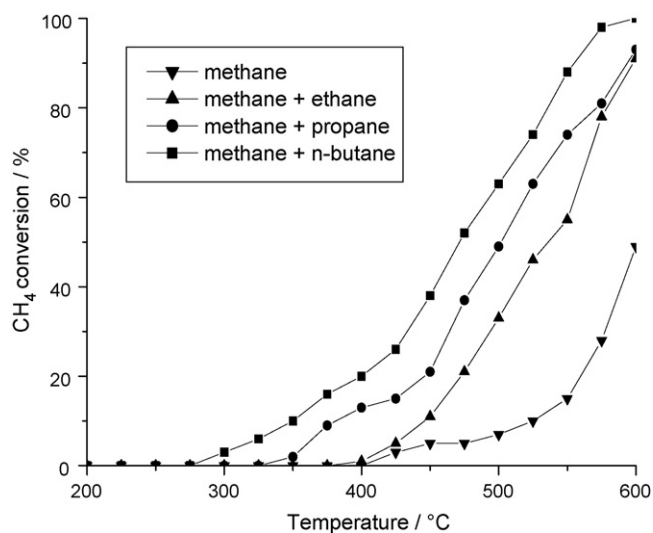

Fig. 1. Methane conversion as a function of temperature on the CH_4–O_2 reaction (▼) over pre-sulfated 1% Pt/γ-Al$_2$O$_3$. Effect of C_2H_6 (▲), C_3H_8 (●) and n-C_4H_{10} (■) addition in the reaction feed: 2000 ppmV CH_4, 20% O_2, 50 ppmV SO_2, balance N_2.
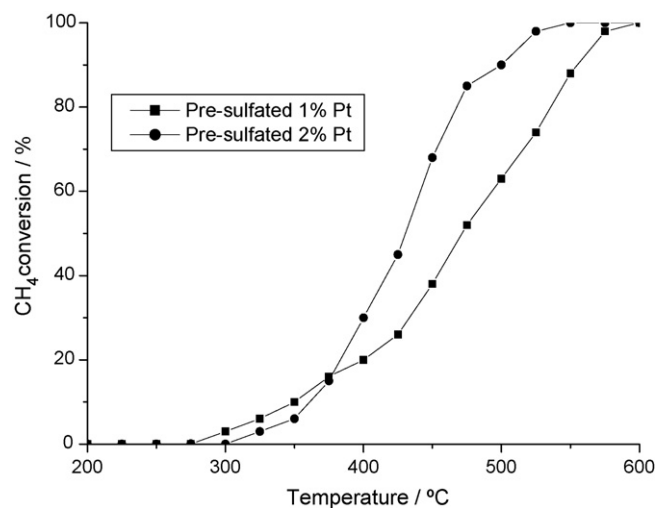
Fig. 2. Methane conversion as a function of temperature on the CH_4–O_2 reaction over pre-sulfated 1% Pt/γ-Al$_2$O$_3$ (■) and pre-sulfated 2% Pt/γ-Al$_2$O$_3$ (●). Reaction feed: 2000 ppmV CH_4, 2000 ppmV n-C_4H_{10}, 20% O_2, 50 ppmV SO_2, balance N_2.

Table 3
Binding energies (eV) of core electrons of Pt $4d_{5/2}$ in pre-sulfated 1% Pt/γ-Al$_2$O$_3$ and pre-sulfated 2% Pt/γ-Al$_2$O$_3$ catalysts

Catalyst (pre-sulfated)	Al 2p	Pt $4d_{5/2}$[a]	S 2p
1% Pt/γ-Al$_2$O$_3$	74.5	315.4 (49)	168.9
		318.5 (51)	
2% Pt/γ-Al$_2$O$_3$	74.5	315.4 (51)	168.9
		318.5 (49)	

[a] In parenthesis are peak percentages.

were constant for both catalysts. The binding energy of the S $2p_{3/2}$ (168.9 eV) revealed that S is only present as S^{6+}, thus only sulfate species are present in the catalyst [25].
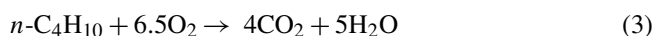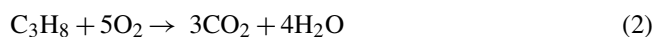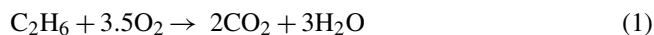
In Table 4 the atomic surface ratios of the pre-sulfated catalysts determined by XPS are indicated. In this table, it can be seen that the Pt/Al XPS signal ratio increases with Pt content in the catalyst.

4. Discussion

Figs. 1 and 2 and Table 2 indicate the effect of C$_2$H$_6$, C$_3$H$_8$, or n-C$_4$H$_{10}$ on CH$_4$–O$_2$ reaction over pre-sulfated 1% Pt/γ-Al$_2$O$_3$ and pre-sulfated 2% Pt/γ-Al$_2$O$_3$.

The increase of methane oxidation rate due to the presence of C$_2$H$_6$, C$_3$H$_8$, or n-C$_4$H$_{10}$ is explained considering two facts:

- The exothermic combustions of C$_2$H$_6$, C$_3$H$_8$, or n-C$_4$H$_{10}$ [20], which initiate at lower temperatures, relative to methane combustion generate large amounts of energy according to the following reactions:

$$C_2H_6 + 3.5O_2 \rightarrow 2CO_2 + 3H_2O \tag{1}$$

$$C_3H_8 + 5O_2 \rightarrow 3CO_2 + 4H_2O \tag{2}$$

$$n\text{-}C_4H_{10} + 6.5O_2 \rightarrow 4CO_2 + 5H_2O \tag{3}$$

The energy generated during the combustion of C$_2$H$_6$, C$_3$H$_8$, or n-C$_4$H$_{10}$ may be transferred to activate the rate determining step of CH$_4$ oxidation, over the catalyst surface, increasing the reaction rate at lower temperatures, according to the mechanism proposed by Burch et al. [26] and Garetto and Apesteguia [27]. These authors interpreted the methane oxidation mechanism in terms of Mars–van Kravelen reduction–oxidation pathways, where the rate determining step is the abstraction of the first hydrogen on the adsorbed methane molecule:

$$CH_4 \cdot L + O \cdot L \xrightarrow{k} CH_3 \cdot L + OH \cdot L \tag{4}$$
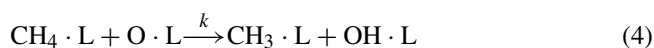
L is an active site.

Table 4
Atomic surface ratios of pre-sulfated 1% Pt/γ-Al$_2$O$_3$ and pre-sulfated 2% Pt/γ-Al$_2$O$_3$ catalysts determined by XPS

Catalyst (pre-sulfated)	Pt/Al
1% Pt/γ-Al$_2$O$_3$	0.0014
2% Pt/γ-Al$_2$O$_3$	0.0030

Thus, C$_2$H$_6$, C$_3$H$_8$, or n-C$_4$H$_{10}$ combustion heat may be largely transferred to reach the activation energy needed to abstract this first hydrogen. This assumption is in agreement with the results presented in Table 2. In this table it can be observed that the promotional effect of the alkane added on CH$_4$ oxidation increases as a function of the alkane combustion heat values [20]. Moreover, Table 2 also shows that this promotional effect increased as a function of the alkane concentration. The energy generated during alkane combustion increased as a function of the alkane molecules concentration.

- On the other hand, C$_2$H$_6$, C$_3$H$_8$, or n-C$_4$H$_{10}$ oxidation may lower the coverage of oxygen on the Pt surface, leaving surface active sites L free for CH$_4$ adsorption, thus increasing its oxidation rate, since, oxygen species inhibit the reaction at full coverage [26]. It is worth noting that the promotional effect of the presence of the alkane added on CH$_4$ oxidation increases as a function of the number of moles of oxygen necessary for the oxidation per-mole of the alkane (according to reactions 1, 2, and 3).

It is well known that the oxidation of SO$_2$ to SO$_3$ is catalyzed by Pt at temperatures greater than 200 °C [28–30] according to the following reaction:

$$SO_2 + O \cdot L \rightarrow SO_3 \tag{5}$$

This reaction over oxygen-covered Pt may cause the removal of surface oxygen, thus may also facilitate adsorption of CH$_4$, resulting in a further increase in the CH$_4$ conversion. The promoting effect of the oxidation of SO$_2$ to SO$_3$ on methane oxidation may be the same in the presence or in the absence of alkanes.

Now, results presented in Fig. 2 and Table 2 reveal that increasing Pt content in the catalyst resulted in a further strong increase of the catalytic activity for methane combustion in the presence of 2000 ppmV n-butane in the reaction feed. This enhancement cannot be due to a change in platinum dispersion, since both catalysts have similar dispersion values. This enhancement cannot be due to a change of the oxidation state of Pt surface atoms, since both catalysts revealed the same binding energy values of Pt species (Table 3). This enhancement cannot be due to a change in sulfates concentration, since both catalysts have similar amounts of sulfates (Table 1). However, in Table 1 it can be seen that the number of Pt surface sites is higher in 2% Pt/γ-Al$_2$O$_3$ relative to 1% Pt/γ-Al$_2$O$_3$. This result is in agreement with the values of the atomic surface ratios determined by XPS of the catalysts (Table 4), showing an increase in Pt surface atoms as the Pt content increased. The increase in Pt surface sites results in a higher number of Pt surface active sites L for CH$_4$ adsorption according to reaction (4). Thus the probability of CH$_4$ adsorption increases and may result in an increase in the oxidation rate for CH$_4$–O$_2$ reaction.

5. Conclusions

Results obtained in this investigation demonstrated the promoting effect of the presence of C$_2$H$_6$, C$_3$H$_8$, or n-C$_4$H$_{10}$ in the

activation of methane oxidation over pre-sulfated $Pt/\gamma\text{-}Al_2O_3$ catalysts in CH_4–O_2–SO_2 reactions. This promoting effect is explained on basis of the following facts: (i) C_2H_6, C_3H_8, or $n\text{-}C_4H_{10}$ combustion heat may be transferred to activate the CH_4 dissociative adsorption over the catalyst surface increasing methane oxidation rate at lower temperatures; (ii) C_2H_6, C_3H_8, or $n\text{-}C_4H_{10}$ oxidation may lower the coverage of oxygen on the Pt surface, leaving surface active sites free for CH_4 adsorption; (iii) the increase in Pt content in the catalyst results in an increase in Pt surface active sites for CH_4 adsorption, thus the probability of CH_4 adsorption increases and may result in an increase in surface Pt sites oxidation rate for CH_4–O_2 reaction.

The results presented in this investigation suggest that the combination of both promoting effects described (i) addition of C_2H_6, C_3H_8, or $n\text{-}C_4H_{10}$ in the gas feed and (ii) increase of the Pt content (thus increase in the number of Pt surface active sites) may lead to a catalytic system having a very high activity for complete methane oxidation at low temperature. Such new catalytic process may eliminate low concentrations of methane emissions from lean-burn NGV exhausts.

Acknowledgements

References

[1] P. Gelin, M. Primet, Appl. Catal. B: Environ. 39 (2002) 1.
[2] L. Ning, A. Wang, X. Wang, M. Zheng, R. Cheng, T. Zhang, Appl. Catal. 48 (2004) 259.
[3] D. Roth, P. Gelin, E. Tena, M. Primet, Top. Catal. 16 (2001) 77.
[4] C.F. Cullis, B.M. Willatt, J. Catal. 83 (1983) 267.
[5] S. Park, H.J. Hwang, J. Moon, Catal. Lett. 87 (2003) 219.
[6] J.A. Lampert, M.S. Kazi, R.J. Farrauto, Appl. Catal. B: Environ. 14 (1997) 211.
[7] D.L. Mowery, M. Grabosky, T.R. Ahno, R. McCormick, Appl. Catal. B: Environ. 21 (1999) 157.
[8] D.L. Mowery, R.L. McCormick, Appl. Catal. B: Environ. 34 (2001) 287.
[9] J.K. Lampbert, M.S. Kazi, R.J. Farrauto, SAE 961971 (1996) 15.
[10] P. Gelin, L. Urfels, M. Primet, E. Tena, Catal. Today 83 (2003) 45.
[11] R. Burch, D.J. Crittle, B.W.L. Southward, J.A. Sullivan, Catal. Lett. 72 (2001) 153.
[12] J.M. Jones, A. Dupont, R. Brydson, D.J. Fullerton, N.S. Nasri, A.B. Ross, A.V.K. Westwood, Catal. Today 81 (2003) 589.
[13] V. Meeyoo, D.L. Trimm, N.W. Cant, Appl. Catal. B: Environ. 16 (1998) L101.
[14] S. Ordonez, P. Hurtado, H. Sastre, F.V. Diez, Appl. Catal. A: Gen. 259 (2004) 41.
[15] K. Persson, A. Ersson, K. Jansson, N. Iverlund, S. Jaras, J. Catal. 231 (2005) 139.
[16] K. Persson, A. Ersson, K. Jansson, J.L.G. Fierro, S.C. Jaras, J. Catal. 243 (2006) 14.
[17] G. Corro, J.L.G. Fierro, O. Vazquez, Catal. Commun. 6 (2005) 287.
[18] G. Corro, J.L.G. Fierro, O. Vazquez, Catal. Commun. 7 (2006) 436.
[19] F. Arosio, S. Colussi, G. Groppi, A. Trovarelli, Catal. Today 117 (2006) 569.
[20] J.M. Smith, H.C. Van Ness, Thermodynamics, McGraw-Hill, Mexico, 1990.
[21] B. Pawelee, R. Mariscal, R.M. Navarro, S. van Bokhorst, S. Rojas, J.L.G. Fierro, Appl. Catal. A 225 (2002) 223.
[22] E. Czaran, J. Finster, K.H. Schnabel, Z. Anorg. Allg. Chem. 443 (1978) 175.
[23] Z. Zsoldos, L. Guczi, J. Phys. Chem. 96 (1992) 23.
[24] L. Guczi, A. Sarkany, Z. Koppany, Appl. Catal. 120 (1994) L1.
[25] D. Briggs, M.P. Seah (Eds.), Practical Surface Analysis by Auger and X-ray Photoelectron Spectroscopy, 2nd ed., Wiley Chichester, UK, 1990.
[26] R. Burch, D.J. Crittle, M.J. Hayes, Catal. Today 47 (1999) 229.
[27] T.F. Garetto, C.R. Apesteguia, Catal. Today 62 (2000) 189.
[28] G.C. Bond, Catalysis by Metals, Academic Press, London, 1962.
[29] G.I. Godolets, Stud. Surf. Sci. Catal. 15 (1983) 365.
[30] D.D. Beck, M.H. Krueger, D.R. Monroe, SAE, 1991 (Paper no. 910844).